Unusual Cu^{II} and Mn^{II} Complexes of Phenol-Based Ligands Containing Amine, Pyridine and Formyl Functions: Unexpected Structural Features and Solution Studies

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The phenol-based ligand Hpy2ald containing formyl, amine and pyridine functions reacts with copper(II) nitrate, copper(II) bromide and manganese(II) chloride to yield complexes with unexpected structures. In contrast to previously reported coordination compounds with similar ligands, the carbonyl group of the ligand in all complexes does not coordinate to the metal ions. The metal-to-ligand ratio is 2:1 in the case of the copper(II) nitrate complex and 1:1 in the case of the copper(II) bromide and manganese(II) chloride complexes. The copper(II) nitrate complex exhibits both donor-atom and coordination number asymmetry, as one copper ion is pentacoordinate with an N_3O_2 donor set, and the other one is hexacoordinate with an O_6 donor set. In the latter two complexes, the phenol group of the ligand remains protonated and fails to bridge the two metal ions; instead it is semi-coordinated to only one metal ion. This results in the formation of mononuclear complexes in which copper(II) or manganese(II) ions have a distorted square-pyramidal surrounding. All complexes were structurally, spectroscopically and magnetically investigated.

Introduction

Dinucleating phenol-based ligands, which are able to bind two metal ions simultaneously, have attracted significant attention from scientists in the past few years.[1−5] Interest in this topic is due partly to the presence of a dinuclear metal core in many proteins and enzymes. A large number of complexes with phenol-based ligands have been synthesized to mimic dimetallic biosites.[6−8] In addition, interest in this type of complex is also driven by their attractive catalytic[9,10] and magnetic[11−13] properties.

The recognition of the asymmetric nature of many dinuclear biosites has led to the synthesis of a variety of dinucleating ligands bearing adjacent, but dissimilar, donor sets. These ligands have been collectively termed "compartmental". Some time ago, Adams et al. reported an unexpected nickel-induced hydrolysis of unsymmetrical Schiff base compartmental ligands,[2,14] which resulted in the transformation of the imino group of the ligands into a formyl moiety. As this hydrolysis only occurred when nickel(II) salts with non- or weakly coordinating anions were used, it was suggested that the presence of such anions, as well as nickel ions, is crucial.[14]

All the dinuclear complexes obtained with these in situ generated ligands were found to have very similar crystal structures, comprising a dimetallic core with two bridging phenolato groups from two ligands. In all cases the metal-to-ligand ratio was found to be 2:2. The coordination environment around each metal ion was completed by three nitrogen donor atoms from an amino arm of the ligand and an oxygen atom of the formyl group, formed by hydrolysis, to give a distorted octahedron.

In the present study, three novel complexes of the phenol-based compartmental ligand Hpy2ald (Figure 1), containing formyl, amino and pyridine functions, with copper(II) nitrate and bromide, and manganese(II) chloride are reported. The ligand Hpy2ald was prepared as an intermedi-

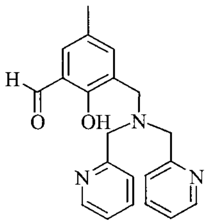

Figure 1. The phenol-based ligand Hpy2ald, containing the tridentate arm in the 2-position and the carbonyl group in the 6-position of the aromatic ring

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ate in the synthesis of asymmetric dinucleating ligands.[15] In contrast to the coordination compounds reported by Adams et al.,[2,14] the present complexes do not possess dinuclear cores comprised of two metal ions and two ligands. In all complexes, the carbonyl group of the ligand does not coordinate to the metal ions, which partly originates from the presence of a stronger nitrate, bromide or chloride donor anion. The metal-to-ligand ratio was found to be 2:1 for the nitrate complex and 1:1 for the bromide and chloride complexes. The crystal structures, spectroscopic and magnetic properties of all three complexes are reported.

Results and Discussion

General

The phenol-based ligand Hpy2ald contains a tridentate arm in the 6′-position, and a carbonyl group in the 2′-position of the phenol ring. Quite similar ligands and their Ni^{II} coordination compounds were previously described by Adams et al.[2] In the overwhelming majority of cases, the ligands reported by Adams were formed in situ by the hydrolysis of an imino arm of the initially dinucleating phenol-based ligands.[2] The structures of the previously described complexes with this type of ligand include dinuclear metal cores, where two metals are doubly bridged by two phenolato groups. In all cases, the C=O group of the ligand is coordinated to the metal ion.[2]

In the present study, three new copper(II) and manganese(II) complexes with the ligand Hpy2ald are reported, each possessing quite different structures. The reaction of Hpy2ald with copper(II) nitrate yields the asymmetric dinuclear complex [Cu_2(py2ald)(μ-NO_3)(NO_3)$_2$]·CH_3CN (Figure 2), in which the two metal ions are doubly bridged by a deprotonated cresolate anion and a didentate nitrate anion. The metal-to-ligand ratio in this complex is 2:1, and the octahedral coordination environment of one of the copper ions is completed by chelating nitrate anions. The aldehyde group of the ligand remains non-coordinated.

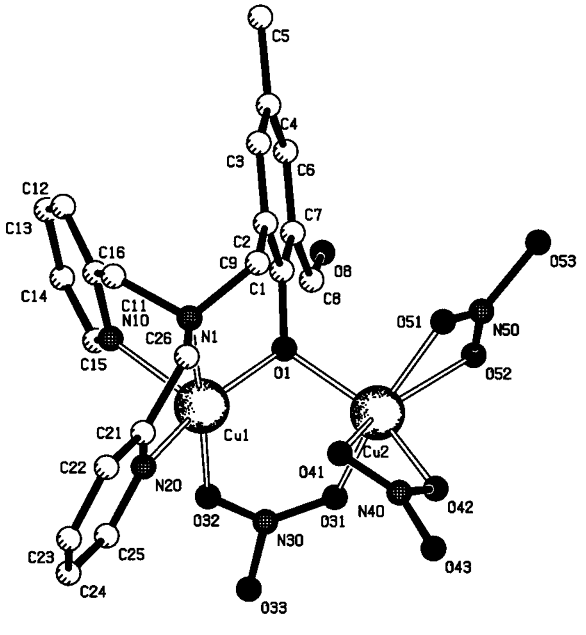

Figure 2. Platon[33] projection of the crystal structure of [Cu_2(py2ald)(μ-NO_3)(NO_3)$_2$]·CH_3CN; hydrogen atoms are omitted for clarity

The reaction of Hpy2ald with $CuBr_2$ yields a mononuclear complex with the formal composition [Cu(Hpy2ald)Br_2]·0.5H_2O. In the crystal, the copper complexes form dimers by hydrogen bonding with the lattice water molecules as hydrogen bond donors and the coordinated bromides as acceptors (Figure 3). The metal to ligand ratio within a mononuclear fragment is 1:1. In this complex, the phenol group of the ligand remains protonated, failing to bridge two metal ions and instead being only semi-coordinated to one metal. As in the case of the nitrate complex, the aldehyde group is not coordinated, but instead is hydrogen-bonded to the protonated phenol. The octahedral coordination environment around the metal ion is completed by nitrogen donor atoms of the tridentate arm from the ligand and two bromide anions.

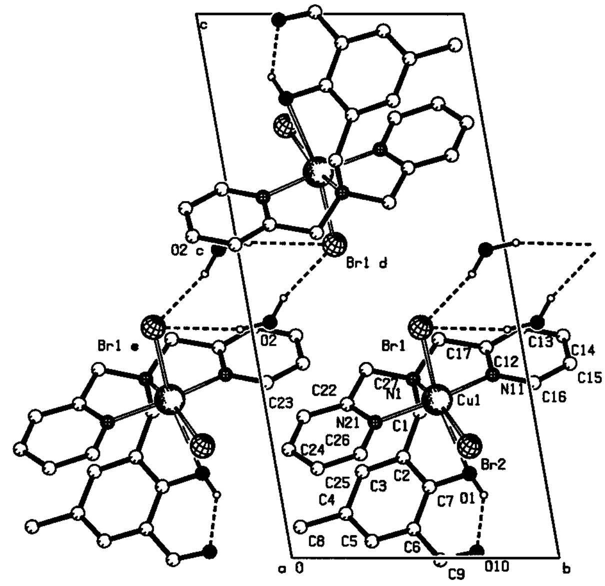

Figure 3. Platon[33] projection of the crystal structure of [Cu(Hpy2ald)Br_2]·0.5H_2O; the occupancy factor of each water molecule is 0.50; only the hydrogen atoms participating in hydrogen bonding are shown

Finally, the reaction of Hpy2ald with manganese(II) chloride yields the complex [Mn(Hpy2ald)Cl]$_2$. The molecular structure of this complex is very similar to the structure of the copper(II) bromide complex with intramolecular hydrogen bonding, but in the crystal lattice no intermolecular hydrogen bonding is present.

These unusual structural features of the three complexes open the possibility to speculate that the structure of complexes with carbonyl-containing phenol-based ligands is largely determined by the donor properties of the anion. Due to the presence of a very weak donor carbonyl group in the ligand, the counterions present in the solution may compete with the oxygen atom of the carbonyl group for a place in the coordination sphere of the metal ion. Thus, a dinuclear core comprised of two metal ions and two ligands, in which the carbonyl group is coordinated to the metal ions, can only be formed if non-coordinating, or very weakly coordinating, anions are present in the solution. This hypothesis is supported by the fact that reaction of Hpy2ald with perchlorate or tetrafluoroborate metal salts yields complexes with structures[16] very similar to those described by Adams.[2] At the same time, stronger donors, such as nitrate and halogen anions, prevent a weaker donor — the carbonyl group — from coordinating to the metal ion. In addition, in all cases, changing the initial ratio of the reactants did not influence the structure of the formed complexes.

Crystal Structure Descriptions

[Cu_2(py2ald)(μ-NO_3-O,O′)(NO_3-O,O′)$_2$]·CH_3CN (1)

A molecular plot of [Cu_2(py2ald)(μ-NO_3)(NO_3)$_2$]·CH_3CN is shown in Figure 2. Selected bond lengths and angles are given in Table 1. The dinuclear core consists of two copper ions [Cu$\cdots$Cu distance 3.0652(6) Å], bridged on one side by an endogenous (μ-phenoxo) bridge and on the other side by an exogenous didentate nitrate anion. The complex shows both coordination-number and donor-atom asymmetry. Cu1 is five-coordinate with an almost ideal square-pyramidal geometry (the parameter τ, which is used to describe the percentage of trigonal distortion from a square-pyramidal geometry, is 0.07 for the Cu1 ion; τ is zero for an ideal square pyramid and one for an ideal trigonal bipyramid),[17] and an N_3O_2 donor set. The basal plane contains two *cis*-located oxygen atoms, O1 from the deprotonated cresolate and O32 from the bridging nitrate anion, and two *cis*-located nitrogen atoms, N1 of the tertiary amine group and N20 of the pyridine ring. The nitrogen atom N10 from the other pyridine ring occupies the apical position. The interior angles of the basal plane vary between 82.07(9)° and 93.06(8)°. The distance Cu1$\cdots$O41 is 3.031(3) Å and is thus too long to consider the O41 atom as the sixth ligand for the Cu1 ion.

Table 1. Selected bond lengths and angles for [Cu_2(py2ald)(μ-NO_3)(NO_3)$_2$]·CH_3CN

Bond lengths (Å)			
Cu1−O1	1.9918(19)	Cu2−O1	1.959(2)
Cu1−O32	1.937(2)	Cu2−O31	1.945(2)
Cu1−N1	2.041(2)	Cu2−O41	2.585(3)
Cu1−N10	2.199(2)	Cu2−O42	1.946(2)
Cu1−N20	1.999(2)	Cu2−O51	1.978(2)
Cu1$\cdots$O41	3.031(3)	Cu2−O52	2.479(3)
Bond angles (°)			
O1−Cu1−O32	92.46(8)	O1−Cu2−O31	90.63(9)
O1−Cu1−N1	93.06(8)	O1−Cu2−O41	96.70(8)
O1−Cu1−N10	89.20(8)	O1−Cu2−O42	151.99(9)
O1−Cu1−N20	163.73(9)	O1−Cu2−O51	93.75(9)
O32−Cu1−N1	174.17(9)	O51−Cu2−O52	57.90(8)
O32−Cu1−N10	99.34(9)	O1−Cu2−O52	101.69(8)
O32−Cu1−N20	92.11(9)	O31−Cu2−O41	103.36(8)
N1−Cu1−N10	82.59(9)	O31−Cu2−O42	90.26(10)
N1−Cu1−N20	82.07(9)	O31−Cu2−O51	158.59(9)
N10−Cu1−N20	105.44(9)	O31−Cu2−O52	100.68(8)
Cu1−O1−Cu2	101.75(9)	O41−Cu2−O42	55.99(10)
		O41−Cu2−O51	96.94(8)
		O41−Cu2−O52	149.42(9)
		O42−Cu2−O51	95.55(10)
		O42−Cu2−O52	105.63(10)

The Cu2 ion is six-coordinate with a very distorted octahedral geometry and an O_6 donor set. Only one of the oxygen atoms belongs to the ligand: the other five are from three different nitrate anions. Two oxygen atoms (O41 and O52) from the two didentate chelating nitrate ions occupy the axial positions, with long Cu−O bonds of 2.585(3) Å and 2.479(3) Å, respectively. The O41−Cu2−O52 angle is only 149.42(9)°, indicating a very large distortion from the regular octahedral geometry, apparently imposed by the small bite angle of the nitrate anions. The oxygen atoms (O42 and O51) of two didentate chelating nitrate anions, the oxygen atom (O1) of the deprotonated cresolate and the oxygen atom (O31) of the didentate bridging nitrate anion lie in the equatorial plane, with Cu−O distances of 1.945(2)−1.978(2) Å. The interior angles of the equatorial plane are somewhat larger than 90°, viz. 90.26(10)−95.55(10)°. One non-coordinated molecule of acetonitrile is present in the crystal lattice.

[Cu(Hpy2ald)Br_2]·0.5H_2O (2)

A molecular plot of the complex is shown in Figure 3. Selected bond lengths and angles are presented in Table 2. As can be evidenced from the picture, the unit cell contains two mononuclear formula units and one water molecule, which appears to be disordered over two positions with an occupancy factor of 0.50. These uncoordinated water molecules act as hydrogen bond donors with coordinated bromide anions as acceptors (see Table 3), thus resulting in the formation of centrosymmetric dimers with the formal composition [Cu(Hpy2ald)Br_2]$_2$·H_2O.

Table 2. Selected bond lengths and bond angles for [Cu(Hpy2ald)Br_2]·0.5H_2O

Bond lengths (Å)			
Cu1−Br1	2.7278(4)		
Cu1−Br2	2.4299(4)		
Cu1−O1	2.932(2)		
Cu1−N1	2.0815(19)		
Cu1−N11	2.0170(19)		
Cu1−N21	2.0246(19)		
Bond angles (°)			
Br1−Cu1−Br2	99.197(12)	Br2−Cu1−N21	97.42(6)
Br1−Cu1−O1	170.75(4)	O1−Cu1−N1	82.40(7)
Br1−Cu1−N1	100.65(5)	O1−Cu1−N11	78.43(7)
Br1−Cu1−N11	93.34(6)	O1−Cu1−N21	95.50(7)
Br1−Cu1−N21	93.63(5)	N1−Cu1−N11	81.03(8)
Br2−Cu1−O1	78.04(5)	N1−Cu1−N21	81.05(8)
Br2−Cu1−N1	160.15(5)	N11−Cu1−N21	161.69(8)
Br2−Cu1−N11	98.15(6)		

Table 3. Selected bond lengths and angles for [Mn(Hpy2ald)Cl_2]

Bond lengths (Å)	
Mn1−Cl1	2.3737(9)
Mn1−Cl2	2.4078(8)
Mn1−O31	2.793(2)
Mn1−N1	2.360(2)
Mn1−N11	2.217(2)
Mn1−N21	2.223(2)

Bond angles (°)			
Cl1−Mn1−Cl2	106.07(3)	Cl2−Mn1−N21	94.92(6)
Cl1−Mn1−O31	76.21(5)	O31−Mn1−N1	75.92(7)
Cl1−Mn1−N1	151.89(5)	O31−Mn1−N11	78.07(7)
Cl1−Mn1−N11	104.33(6)	O31−Mn1−N21	88.15(7)
Cl1−Mn1−N21	102.28(6)	N1−Mn1−N11	73.27(8)
Cl2−Mn1−O31	175.64(5)	N1−Mn1−N21	73.22(7)
Cl2−Mn1−N1	101.98(5)	N11−Mn1−N21	145.95(8)
Cl2−Mn1−N11	97.70(6)		

The coordination environment around the copper(II) ion can best be described as either a very distorted octahedron with a Br_2N_3O donor set, or a square pyramid with a Br_2N_3 donor set and a loosely bound phenol group. The phenol group of the cresol ring remains protonated, which prevents it from forming a bridge between the two copper ions. This, in turn, results in the formation of a mononuclear complex. The oxygen atom (O1) from the phenol group can thus be best regarded as being only semi-coordinated to the Cu1 ion, with a very long Cu−O distance of 2.932(2) Å. It lies in one of the apical positions of an imaginary octahedron, with the second apical position being occupied by one of the bromide anions at a Cu1−Br1 distance of 2.7278(4) Å. The O1−Cu1−Br1 angle is 170.75(4)°. The equatorial plane is formed by the second bromide anion (Br2), the nitrogen atom (N1) from the tertiary amine group, and two nitrogen atoms (N11 and N21) from the pyridine rings. The pyridine rings are located on either side of the ligand plane, and are thus *trans* to each other. The interior angles N1−Cu1−N11 and N1−Cu1−N21 are smaller than 90° [81.03(8)° and 81.05(8)°, respectively], due to the constraints imposed by the three-bond ligand-bite.

Besides the intermolecular hydrogen bonding, an intramolecular hydrogen bond is realized between the cresolic proton and the oxygen atom from the formyl group (the O1···O10 distance is 2.645 Å, see also Table 4).

[Mn(Hpy2ald)Cl_2] (3)

A molecular plot of the complex is shown in Figure 4. Selected bond lengths and angles are presented in Table 3. The structure of the complex is very similar to that of complex **2**. However, in this case no intermolecular hydrogen bonding is present between the formula units. The coordination environment around the Mn1 ion can best be described as a very distorted octahedron. The chloride anion (Cl2) and the oxygen atom (O31) from the cresol group occupy the axial positions. Although the Mn1−O31 distance of 2.793(2) Å is shorter than the respective distance in complex **2** [2.932(2) Å], the oxygen atom can still be best regarded as being only semi-coordinated to the manganese ion. Similarly to the copper(II) bromide complex, the OH group of the cresolic moiety remains protonated. The Cl2−Mn1−O31 angle is 175.64(5)°. The basal plane of the octahedron is formed by two nitrogen atoms (N11 and N21) from two pyridine rings, the nitrogen atom (N1) from the tertiary amine group and the chloride anion (Cl1). The

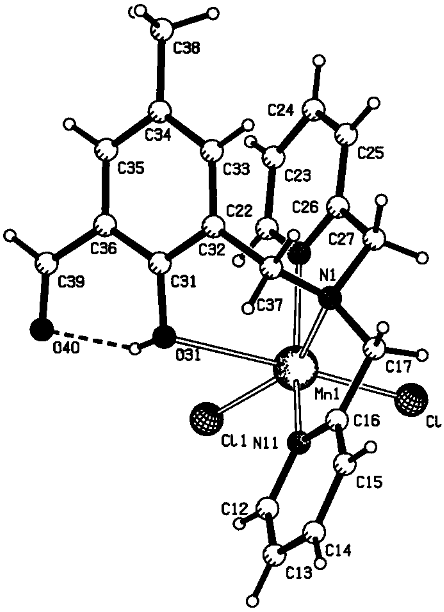

Figure 4. Platon[33] projection of the crystal structure of [Mn(Hpy2ald)Cl_2]

Table 4. Hydrogen bonds D−H···A for [Cu(Hpy2ald)Br_2]$_2$·H_2O and [Mn(Hpy2ald)Cl_2]

	Donor−H···Acceptor	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (°)
	O1−H10···O10	1.00(5)	1.82(5)	2.645(3)	137(4)
[Cu(Hpy2ald)Br_2]·0.5H_2O	O2−H20···Br1[a]	0.99	2.44	3.405(4)	164.2
	O2−H30···Br1	0.95	2.70	3.592(4)	155.3
[Mn(Hpy2ald)Cl_2]	O31−H1O···O40	0.72(3)	2.01(3)	2.660(3)	151(4)

[a] $2 - x, 1 - y, 1 - z$.

Mn−N distances vary in the range 2.217(2)−2.360(2) Å, and the Mn1−Cl1 distance is 2.3737(9) Å. An intramolecular hydrogen bond is realized between the hydrogen atom of the cresolic group and the oxygen atom from the formyl group, with an O31···O40 distance of 2.660 Å (Table 4).

Physical Characterization

Mass Spectroscopy

The mass spectra (ESI-MS) of [Cu(Hpy2ald)Br$_2$]·H$_2$O and [Mn(Hpy2ald)Cl$_2$], both recorded in methanol, are characterized by one major peak corresponding to the moiety [M(Hpy2ald)X]$^+$ (*m*/*z* = 491 for [Cu(Hpy2ald)Br]$^+$ and *m*/*z* = 437 for [Mn(Hpy2ald)Cl]$^+$). These results are as expected and indicate that the solid-state structures of both complexes are retained in solution. However, if the mass spectrum of [Mn(Hpy2ald)Cl$_2$] is recorded again after one week in solution, two new peaks appear in the spectrum, at the expense of the original ones, at *m*/*z* = 362 and *m*/*z* = 451. The first of them was tentatively assigned to the product of an oxidation of the formyl group of the ligand to the respective carboxylate group. The theoretically calculated isotope pattern for the formula $C_{21}H_{20}N_3O_3$ (corresponding to the ligand with the carboxylic group instead of a formyl moiety) is in a good agreement with the experimentally observed one. Assuming the first assumption is correct, the peak at *m*/*z* = 451 should correspond to the complex of composition [MnL′Cl]$^+$, where L′ is the oxidized ligand. Interestingly, the oxidation of the ligand was only observed for the manganese complex, but not for the copper complexes.

The mass spectra of [Cu$_2$(py2ald)(μ-NO$_3$)(NO$_3$)$_2$] were recorded for comparison in two different solvents (acetonitrile and methanol). The spectrum of the complex in acetonitrile solution shows two major peaks. The most intense one, at *m*/*z* = 596, corresponds to the fragment [Cu$_2$(py2ald)(NO$_3$)$_2$]$^+$, in agreement with the solid-state structure of the complex. However, the second peak in the spectrum, whose intensity is only slightly lower (relative abundance 95%) at *m*/*z* = 472, corresponds to the mononuclear fragment [Cu(Hpy2ald)NO$_3$]$^+$. The discrimination between mononuclear and dinuclear fragments is unambiguous from the difference in observed isotopic patterns, caused by the presence of one or two copper ions. The structure of the latter complex can be expected to look similar to the structure of the copper bromide complex, with the phenol group of the ligand being still protonated. When the spectrum of the complex is recorded in methanol solution, the peak corresponding to the mononuclear fragment [Cu(Hpy2ald)(NO$_3$)(CH$_3$OH)$_2$]$^+$ becomes the most intense, while the intensity of the peak corresponding to the dinuclear moiety diminishes significantly (relative abundance 60%). The results of mass spectroscopy prompted us to suggest that, in solution, the dinuclear complex with the deprotonated ligand exists in equilibrium with the mononuclear complex with the protonated ligand, and this equilibrium is shifted towards the mononuclear complex in a methanol solution.

Ligand-Field Spectroscopy

Ligand-field spectra of all complexes were recorded in the solid state, as well as in solution (methanol for complexes **2** and **3** and acetonitrile and methanol for complex **1**). The ligand-field spectrum of complex **1** in the solid state (diffuse reflectance) is characterized by two major peaks. The first one, at 418 nm, corresponds to the LMCT transition of the phenolate group to the copper ions.[6] The second peak, at 640 nm, is in a normal range for d-d transitions of Cu^{II} ions.[18] In the diffuse reflectance spectrum of complex **2**, a fairly broad peak corresponding to a d-d transition is observed at 750 nm, with a shoulder around 940 nm. As shown previously, such spectroscopic behavior (high-energy absorption band in the visible region with a low-energy shoulder) is typical for square-pyramidal copper(II) complexes.[19] Thus the coordination sphere around the metal center can indeed be best described as square pyramidal. Another intense band is observed at 378 nm. Taking into account that the OH group of the ligand is only semi-coordinated to the copper ion, and thus the LMCT band from the OH group to the metal ions is unlikely to be visible, we were forced to assign this band to the charge transfer from the bromide anions to the copper ions. Similarly, in the diffuse reflectance spectrum of complex **3** a band is observed at 356 nm, which was assigned to the charge-transfer band from the chloride anions to the manganese ions. The d-d transition band in octahedrally surrounded Mn^{II} is known to be very weak, and must be hidden by the tail of the LMCT band, which is not uncommon.[18]

When the spectrum of complex **1** in acetonitrile solution is recorded, the position of the d-d transition band shifts only slightly to 672 nm. However, when the spectrum is recorded in methanol, this band shifts significantly (from 640 nm to 719 nm) towards higher wavelengths ("red shift"). These results suggest the change of the coordination sphere around the copper(II) ions in solution, presumably towards a square-pyramidal geometry.[20] This observation appears to be in agreement with the results of mass-spectroscopic measurements, which suggest the presence of significant amounts of mononuclear copper(II) species in methanol solution. The position of the d-d band in the spectrum of complex **1** in methanol solution is quite close to the position of the d-d band in complex **2**, which can be regarded as additional evidence for the presence of a mononuclear species similar in structure to complex **2**.

When the spectrum of complex **2** is taken in methanol solution, the position of the d-d band shifts somewhat towards the UV region (ca. 700 nm). Possible reasons for this shift are the solvation of the copper ions or partial exchange of the bromide anions with methanol molecules. The spectrum of [Mn(Hpy2ald)Cl$_2$] remains unchanged if recorded in methanol. However, after a prolonged time in solution a shift of the LMCT band (ca. 100 nm) towards the IR region is observed, suggesting the oxidation of the ligand, as evidenced by mass-spectroscopic measurements.

EPR Spectroscopy

The EPR spectrum of complex **1**, recorded in the solid state at room temperature, exhibits one fairly broad isotropic signal with $g = 2.15$. No hyperfine splitting is resolved and no triplet signal is detected. The resolution does not improve upon cooling to liquid nitrogen temperature. A very similar spectrum is observed when the measurement is performed on a frozen acetonitrile solution. These data suggest an interaction between two copper(II) centers at relatively close positions, leading to exchange narrowing. However, when the spectrum is recorded in a methanol glass, it becomes much more complicated (Figure 5a). The spectrum obviously indicates the presence of two different species in solution, and can be best regarded as an overlapping superposition of two rhombic spectra. For both species, a ^{63,65}Cu hyperfine splitting can be observed in the g_z region, although some lines are partially hidden either due to the overlapping of two spectra with each other, or in $g_{x,y}$ region. The resulting spectrum was satisfactory simulated[21] (Figure 5b) considering two non-interacting Cu^{II}-containing species in an approximate 1:1 ratio. For the species X, the simulating parameters are $g_x \approx g_y = 2.10$, $g_z = 2.44$, $A_x = 1.1$ mT (11×10^{-4} cm^{-1}), $A_y = 0$, $A_z = 10.9$ mT (124×10^{-4} cm^{-1}), and for the species Y, $g_x \approx g_y = 2.14$, $g_z = 2.26$, $A_x = 0$, $A_y = 0.43$ mT (4×10^{-4} cm^{-1}), and $A_z = 17.2$ mT (182×10^{-4} cm^{-1}). Although the exact interpretation proved to be difficult, these parameters suggest a $d_{x^2-y^2}$ ground state for both species X and species Y. The simulation parameters for species X are characteristic for elongated rhombic octahedral CuO_6 chromophores,[20] and are very close to the values typical for Cu^{II} ions in a methanol glass. The origin of this species could be Cu^{II} ions coordinated by the nitrate anions and/or, at least partially, by methanol molecules. The simulation parameters for the species Y are close to those for square-planar CuN_2O_2 chromophores. Thus, these results are in good agreement with the presence in solution of a mononuclear species [Cu(Hpy2ald)NO$_3$]$^+$, as suggested by mass spectrometry and ligand-field spectroscopy. However, it should be noticed that neither EPR nor ligand-field measurements provide any direct evidence confirming the presence of dinuclear species in solution as well. Thus, although the presence of dinuclear species was evidenced during the mass-spectroscopic measurements, it cannot be directly deduced from other spectroscopic techniques. Therefore we cannot exclude another possibility — the complete dissociation of the dinuclear complex into mononuclear units of composition [Cu(Hpy2ald)NO$_3$]$^+$ in methanol solution.

The EPR spectrum of complex **2** in the solid state has a rhombic character, with $g_x = 2.05$, $g_y = 2.10$ and $g_z = 2.25$, suggesting a $d_{x^2-y^2}$ ground state. When the spectrum is recorded in a methanol glass, hyperfine splitting becomes obvious. Three of four lines are easily observed (Figure 6a), whereas the fourth is partially hidden in the $g_{x,y}$ region. The spectrum was simulated[21] (Figure 6b) using the parameters $g_x = 2.04$, $g_y = 2.06$, $g_z = 2.24$, $A_x \approx A_y \approx 0$ and $A_z = 18.4$ mT (192×10^{-4} cm^{-1}). These data suggest a distorted square-pyramidal environment for the Cu^{II} ions,[22] in agreement with the crystal structure of the complex.

One can also notice an additional peak at high field (approximately 330 mT), with a g-value below 2, in the spectrum of the complex. The appearance of this signal may indicate the presence of a small amount of dinuclear copper(II) species in solution. Although the solid-state structure of the complex is essentially mononuclear, the partial formation of dinuclear species in solution due to the presence of potentially bridging bromide anions can be imagined. In this case, this absorption should originate from a $\Delta M_s = \pm 1$ transition of the triplet spectrum.[6] No signal corresponding to a $\Delta M_s = \pm 2$ transition could be detected. As the structure of these presumably dinuclear species is unknown, the presence of this high-field signal was neglected during the simulation of the spectrum.

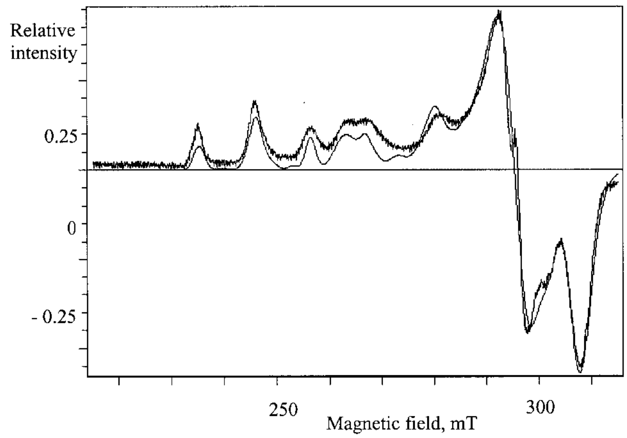

Figure 5. X-band EPR spectrum of: a) [Cu$_2$(py2ald)(NO$_3$)$_3$] (frozen methanol solution, 77 K), and b) simulated curve[21] (see text for further details)

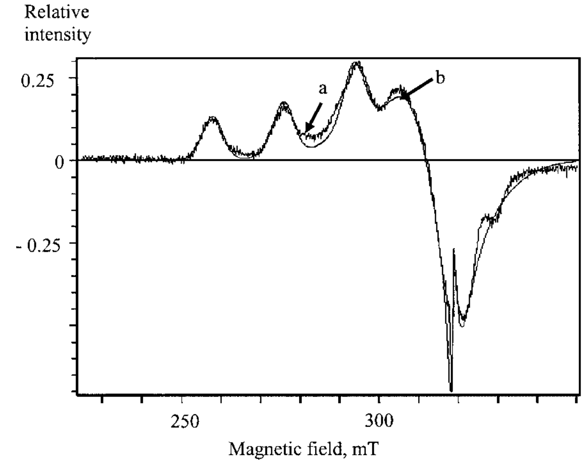

Figure 6. X-band EPR spectrum of: a) [Cu(Hpy2lad)Br$_2$]$_2$·H$_2$O (frozen methanol solution, 77 K), and b) the simulated curve[21] (see text for further details); the sharp signal in the spectrum belongs to the reference DPPH ($g = 2.0036$)

Table 5. Calculated equivalent conductances (ohm^{-1} cm^2 mol^{-1}) of the complexes, measured for 1 mM solutions in acetonitrile (**1**) and in methanol (**1**, **2** and **3**)

	$[Cu_2(py2ald)(NO_3)_3]·CH_3CN$	$[Cu(Hpy2ald)Br_2]·0.5H_2O$	$[Mn(Hpy2ald)Cl_2]$
Acetonitrile	117	–	–
Methanol	160	73	78

The X-band EPR spectrum of the manganese complex **3** in the solid state shows a very broad pattern in the range 0−800 mT. The resolution does not improve upon cooling to 77 K. Such behavior of manganese complexes is not unusual and is caused by zero-field splitting effects.[23] No hyperfine splitting can be observed in the solid-state spectrum, due to dipole-dipole interactions between closely located manganese(II) ions. The spectrum recorded in a frozen methanol solution is much better resolved and shows the usual ^{55}Mn six-line pattern ($A = 9.3$ mT).

Conductivity Measurements

The specific conductivity of 1 mM solutions of the complexes was measured in acetonitrile and methanol for complex **1**, and in methanol for complexes **2** and **3**. The calculated values of equivalent conductances of all three complexes are presented in Table 5. As can be seen, the value of the equivalent conductance for complex **1** in acetonitrile (117 ohm^{-1} cm^2 mol^{-1}) suggests that the complex exists as a 1:1 electrolyte in acetonitrile solution.[24] However, in methanol solution the equivalent conductivity value of 160 ohm^{-1} cm^2 mol^{-1} falls in the range observed for 2:1 electrolytes.[24] These results seem to support the hypothesis about the complete dissociation of the dinuclear complex **1** into mononuclear units in methanol solution, as one would expect the resulting $[Cu(Hpy2ald)(NO_3)_2]$ complex to behave as a 1:2 electrolyte, due to relatively weak bonds between the copper ions and the nitrate groups. The values of the equivalent conductivities obtained for complexes **2** and **3** are very close (Table 5) and suggest that both complexes are 1:1 electrolytes.[24]

Cyclic Voltammetry

The cyclic voltammogram of complex **1**, recorded in an acetonitrile solution while scanning towards the negative region of potentials, is characterized by one quasi-reversible wave ($E_{1/2}$ = -0.31 V, $\Delta E = 0.19$ V, $v = 0.1$ V), which was tentatively assigned to the $Cu^{II,II}/Cu^{II,I}$ redox couple, and one completely irreversible wave at $E_{pc} = -0.60$ V. On the reverse scan, a sharp stripping peak, caused by the redissolution of the copper metal deposited on the electrode, is present. It can therefore be concluded that the second metal-centered reduction is accompanied by the destruction of the complex. This is not surprising, as the coordination of three nitrate anions to the Cu^I ion is unlikely to be possible in this case. In the positive range of potentials, a reversible oxidation wave ($E_{1/2} = 0.81$ V) is observed, corresponding to the one-electron oxidation of the ligand.[6] The cyclic voltammogram recorded in a methanol solution in the negative range of potentials is characterized as well by two successive partially overlapping electrochemical waves. However, they are shifted significantly towards the positive range of potentials and are completely irreversible ($E_{pc} = -0.19$ V and $E_{pc} = -0.28$ V). Similarly to the previous case, the reduction of the copper(II) ions to the copper(I) state is accompanied by the decomposition of the complex and the deposition of the metal on the electrode surface. The positive potential range does not change significantly when recording the voltammogram in a methanol solution.

The cyclic voltammogram of complex **2**, recorded in a methanol solution while scanning towards the negative range of potentials, is characterized by one fully reversible one-electron electrochemical wave, corresponding to the Cu^{II}/Cu^{I} complexed couple ($E_{1/2} = -0.12$ V, $\Delta E = 0.18$ V, $v = 0.1$ V/s). In the positive range of potentials, one irreversible electrochemical wave at $E_{pa} = 1.17$ V is observed, assigned to the ligand oxidation.

The cyclic voltammogram of complex **3** is characterized by only one irreversible oxidation wave at $E_{pa} = 1.20$ V. By comparing the results with the cyclic voltammogram of complex **2**, this electrochemical wave was assigned to the ligand oxidation. No metal-centered electrochemical waves can be observed up to +1.5 V vs. Ag/AgCl electrode, suggesting a very significant stability of the Mn^{II} oxidation state in the complex.

Magnetic Susceptibility

Magnetic susceptibility measurements have been performed on powdered crystals of **1** ($m = 29.11$ mg), **2** ($m = 50.20$ mg) and **3** (19. 04 mg) at 0.1 Tesla. Values for χ in the copper(II) complexes have been calculated for dinuclear species.

At 300 K, the χT value for complex **2** is 0.84 $cm^3·K·mol^{-1}$. This value remains almost constant, as the compound shows Curie−Weiss behavior over the entire temperature region. The Curie constant C_2 is 0.42 $cm^3·K·mol^{-1}$, indicating a g value of 2.12. The Curie temperature θ_2 is 0 K, as expected. Thus no magnetic coupling is present between two mononuclear fragments coupled by the disordered water molecule.

For complex **3**, χT is 4.40 $cm^3·K·mol^{-1}$ at 300 K, corresponding to a magnetic moment of 5.93 μ_B. This value is in perfect agreement with the theoretically expected value for a high-spin Mn^{II} ion ($S = 5/2$). It remains unchanged over the entire temperature range, indicating the paramagnetic behavior of the complex, as could be predicted from the structure of the complex. The Curie temperature θ is 0 K, as expected.

A plot of χ^{-1} and χT vs. temperature for complex **1** between 5 and 150 K (with χ being the magnetization per dinuclear complex) is shown in Figure 7. From the increase of the magnetic susceptibility at low temperature (from $\chi_1 T = 0.89$ cm^3·K·mol^{-1} at 150 K to $\chi_1 T = 1.05$ cm^3·K·mol^{-1} at 5 K) ferromagnetic behavior is evidenced. By linear regression, the Curie constant has been determined to be 0.45 cm^3·K·mol^{-1}, which results in a g value of 2.18. This value is in very good agreement with that determined from EPR measurements in the solid state (g = 2.15).

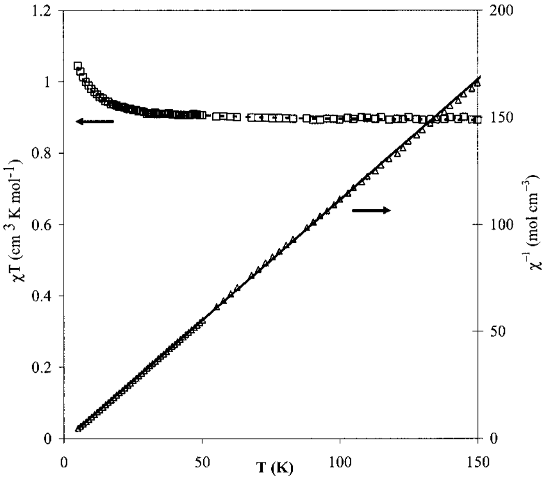

Figure 7. $\chi_1 T$ vs. T (Δ) and χ_1^{-1} vs. T curves (□) of **1**; the solid line represents the linear fitting according to the Curie−Weiss law and the dashed line represents the calculated lines for the parameters J = 3.2 cm^{-1}, g = 2.17 and R = 1.24×10^{-5}

A ferromagnetic interaction is usually observed when the magnetic orbitals of two metal ions have a negligible overlap, whereas an antiferromagnetic exchange is found when the magnetic orbitals are pointing towards each other in such a way that the overlap integral is reasonably large.[25,26] In complex **1**, two unpaired electrons of the Cu1 and Cu2 ions are both occupying $d_{x^2-y^2}$ orbitals. In a symmetrical complex, a bridging phenoxo group with an angle of 101.75(9)° between the copper centers would normally result in an antiferromagnetic interaction. However, due to the asymmetry of the penta- and hexacoordinate copper(II) ions, induced by the ligand Hpy2ald and the nitrate anions, an overlapping of two $d_{x^2-y^2}$ orbitals can be expected to be insignificant. In this case, a weak ferromagnetic exchange can be expected.

The magnetic behavior has been simulated using the Bleaney−Bowers equation[27,28] [see Equation (1)], in which $-J$ is the magnetic exchange parameter and all constants have their usual value.[27]

$$\chi = \frac{2Ng^2\beta^2}{kT[3+\exp(-J/kT)]} \qquad (1)$$

The best simulation is obtained with the values J = 3.2 cm^{-1} and g = 2.17. The reliability factor, defined as $R = n^{-1}[\Sigma(\chi_{obs} - \chi_{cal})^2/(\chi_{cal})^2]$ (n = number of data points) is 1.24×10^{-5}.

Conclusion

In the present study, three new complexes of copper(II) nitrate, copper(II) bromide and manganese(II) chloride with a phenol-based ligand containing a formyl group in the *ortho* position of the phenol ring have been prepared and structurally characterized. The structures of all compounds are very different from previously reported ones with similar ligands. In all cases, the carbonyl group of the ligand does not coordinate to the metal ions. The reaction of copper(II) nitrate with the ligand yields a dinuclear complex [Cu_2(py2ald)(μ-NO_3)(NO_3)$_2$], which possesses both donor-atom asymmetry and coordination-number asymmetry, whereas both copper(II) bromide and manganese(II) chloride form mononuclear complexes of formula [M(Hpy2ald)X_2] (X = Cl or Br). The behavior of the complexes in the solid state and in solution was characterized by means of ligand field and EPR spectroscopy, mass spectrometry, conductivity measurements, cyclic voltammetry and magnetic susceptibility studies. Whereas the coordination environments of the metal ions for the mononuclear complexes appear to be mostly retained upon dissolution, we were able to observe the dissociation of the dinuclear nitrate complex in methanol. Although the results of mass-spectroscopic measurements suggest the existence of mononuclear, as well as dinuclear, species at equilibrium, other spectroscopic techniques, as well as conductivity measurements, do not offer direct evidence for the presence of an initial dinuclear complex in methanol solution. Therefore, the complete dissociation of the initial dinuclear complex into mononuclear units of composition [Cu(Hpy2ald)(NO_3)$_2$], whose structure is expected to be similar to the copper(II) bromide and manganese(II) chloride complexes, can also be suggested. The magnetic susceptibility measurements indicate a ferromagnetic behavior for the nitrate complex and paramagnetic behavior for both the copper chloride and manganese bromide complexes.

Experimental Section

Materials and Methods: All starting materials are commercially available and were used as purchased. The ligand Hpy2ald was synthesized as described previously.[15] The infrared spectra of the complexes in the 4000−300 cm^{-1} range were recorded on a Bruker 330V IR spectrophotometer equipped with a Golden Gate Diamond. The ligand-field spectra of the solids (300−2000 cm^{-1}, diffuse reflectance) and in solution were taken on a Perkin−Elmer 330 spectrophotometer equipped with a data station. Electrospray mass spectra (ESI-MS) in acetonitrile or methanol solution were recorded on a Thermo Finnigan AQA apparatus. X-band electron paramagnetic resonance (EPR) measurements were performed at room temperature and at 77 K in the solid state, or at 77 K as frozen methanol solutions on a Jeol RE2x electron spin resonance spectrometer, using DPPH (g = 2.0036) as a standard. The conductivity measurements were performed using a Philips PW9526 digital conductivity meter and PW 9552/60 measuring cell with 1 mM solutions of the complexes in acetonitrile and/or methanol. Cyclic voltammetry measurements were performed with an Autolab PGSTAT 10 cyclic voltammeter, using a Pt working electrode and a Ag/AgCl reference electrode in acetonitrile or methanol (10^{-3} M), with tetrabutylammonium perchlorate as supporting electrolyte, at a scan rate of 0.1 mV/s. Bulk magnetizations of polycrystalline samples were measured in the range 5−300 K with a Quantum Design MPMS-5S SQUID magnetometer, in a 1 kG applied field. The data were corrected for the experimentally determined contribution of the sample holder. Corrections for the diamagnetic responses of the complexes, as estimated from Pascal's constants, were applied.[29]

The solution studies were performed with either acetonitrile or methanol as solvent in the case of complex **1**, and methanol for complexes **2** and **3**, due to the fact that neither of the two latter complexes is soluble in acetonitrile.

[Cu$_2$(py2ald)(μ-NO$_3$)(NO$_3$)$_2$]·CH$_3$CN (1): 20 mL of an acetonitrile solution of the ligand (56 mg, 0.16 mmol) were added to an equal volume of a copper(II) nitrate solution (77 mg, 32 mmol) in acetonitrile. Slow evaporation of the solvent led to the appearance of green rectangular crystals, which were of sufficient quality for X-ray structure determination. The crystals were found to deteriorate rapidly when taken out of the mother liquor, due to the loss of an acetonitrile molecule. $C_{21}H_{20}Cu_2N_6O_{11}$ (659.5): calcd. C 38.2, H 3.1, N 12.7; found C 37.9, H 3.4, N 12.8. IR: 3047 cm^{-1} (C−H stretching), 1610 (C=O stretching), 1550 (C=C arom., C=N arom.), 1436 (chelating didentate NO_3^-, N=O stretching), 1283 [bridging didentate NO_3^-, $\nu_a(NO_2)$], 998 [bridging didentate NO_3^-, $\nu_s(NO_2)$].

[Cu(Hpy2ald)Br$_2$]·0.5H$_2$O (2): 20 mL of a methanol solution of the ligand (56 mg, 0.16 mmol) were added to an equal volume of a copper(II) bromide solution (72 mg, 0.32 mmol). Green rectangular crystals appeared when the solvent was almost completely evaporated. Their quality was found to be suitable for X-ray diffraction analysis. $C_{42}H_{44}Br_4Cu_2N_6O_5$:calcd. C 43.5, H 3.8, N 7.3; found C 43.9, H 3.8, N 7.5. IR: ca. 3600 cm^{-1}, broad band (H_2O, asymmetric and symmetric OH stretching), 2980 (C−H stretching), 1654 (C=O stretching), 1608 (C=C arom., C=N arom.).

[Mn(Hpy2ald)Cl$_2$] (3): 20 mL of a methanol solution containing manganese(II) chloride dihydrate (129 mg, 0.8 mmol) were added to an equal volume of a methanol solution of the ligand (56 mg, 0.16 mmol). Slow evaporation of the resulting bright-yellow solution gave colorless crystals of the product. These crystals were found to be of sufficient quality for X-ray crystal structure determination. $C_{21}H_{21}Cl_2MnN_3O_2$: calcd. C 53.3, H 4.5, N 8.9; found C 52.9, H 4.9, N 8.9. IR: 2968 cm^{-1} (C−H stretching), 1655 (C=O stretching), 1604 (C=C arom., C=N arom.)

X-ray Crystallographic Study: X-ray intensities were collected on a Nonius−KappaCCD diffractometer with rotating anode (λ = 0.71073 Å, graphite monochromator) at a temperature of 150(2)K up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1}. The structures were solved by direct methods (SHELXS-97,[30] compound **1**) or automated Patterson methods (DIRDIF99,[31] compounds **2** and **3**) and refined with SHELXL-97[32] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The phenolic hydrogen atoms of compounds **2** and **3** were located in the difference Fourier map and refined freely with isotropic displacement parameters. The water hydrogen atoms of compound **2** were located in the difference Fourier map and kept fixed in these positions. All other hydrogen atoms were refined as rigid groups. Illustrations, structure calculations, and structure checking were performed with the PLATON software package.[33] Further crystallographic details are given in Table 6.

CCDC-216684 (**1**), -216685 (**2**), and -216686 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 6. Crystallographic details for complexes **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{21}H_{20}Cu_2N_6O_{11}\cdot C_2H_3N$	$C_{21}H_{21}Br_2CuN_3O_2\cdot 0.5H_2O$	$C_{21}H_{21}Cl_2MnN_3O_2$
Molecular mass	700.56	579.78	473.25
Crystal color	dark green	green	yellow
Crystal size [mm^3]	0.48 × 0.24 × 0.18	0.24 × 0.18 × 0.06	0.56 × 0.15 × 0.03
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a (Å)	8.6632(7)	7.7651(1)	7.6829(14)
b (Å)	17.3510(10)	8.8800(1)	8.8364(11)
c (Å)	19.5299(17)	16.9099(2)	16.329(2)
α (deg.)	90	98.0365(6)	95.936(11)
β (deg.)	97.203(7)	93.0171(7)	92.005(14)
γ (deg.)	90	112.7805(6)	111.789(13)
V (Å^3)	2912.5(4)	1057.19(2)	1020.6(3)
Z	4	2	2
$D_{calcd.}$ (g/cm^3)	1.598	1.821	1.540
μ [mm^{-1}]	1.529	4.838	0.932
Absorption correction	SADABS[34]	PLATON (DELABS)[33]	SADABS[34]
Transmission range	0.61−0.76	0.38−0.79	0.64−0.97
Refl. collected/unique	51234/6695	14345/4758	16182/4640
Parameters/restraints	390/0	276/0	267/0
$R1/wR2$ [$I > 2\sigma(I)$]	0.0408/0.1091	0.0260/0.0595	0.0467/0.1098
$R1/wR2$ [all refl.]	0.0532/0.1172	0.0325/0.0625	0.0755/0.1225
GoF	1.043	1.036	1.037

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