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Synthesis and characterization of copper(I) complexes of dimethyldipicolinate (dmdp) and X-ray structure of the mononuclear six-coordinate complex $[Cu(dmdp)_2]ClO_4$

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Abstract

Copper(I) salts form with dimethyldipicolinate (dmdp) colored diamagnetic complexes of the type Cu(dmdp)X for X = Cl, Br, I, NCO and N_3 and $Cu(dmdp)_2X$ for X = NO_3 and ClO_4. The complexes are characterized by elemental analysis, IR and electronic spectra. The overall physical measurements suggest that dmdp acts as an O,O,N-tridentate chelating ligand in all these complexes. The 1:2 complexes contain ionic nitrate and perchlorate groups, whereas 1:1 complexes contain bridging halide, azide or cyanate ions. The structure of the mononuclear 1:2 copper(I) perchlorate complex, as determined by single crystal X-ray diffraction, consists of a $[Cu(dmdp)_2]^+$ cation and ClO_4^- anion. In the cation, one of the two dmdp molecules coordinates copper(I) by its two carbonyl oxygen and the hetero nitrogen atom whereas the other molecule binds copper(I) via the carbonyl oxygen of one $-CO_2Me$ group and the oxygen atom bonded to the methyl of the other $-CO_2Me$ group leaving free C=O, giving rise to a hexa-coordinate distorted octahedral copper(I) environment. The Cu–O bonds are variable from 2.318(4) to 2.622(5) Å and the Cu–N distances are 1.957(5) and 1.974(5) Å.

Keywords: Copper(I) complexes; Dimethyldipicolinate complexes; Hexa-coordinate copper(I); Synthesis; Spectra; Crystal structures

1. Introduction

The stereochemistry of mononuclear copper(I) complexes is dominated by four-coordinate species, but significant numbers of two- and three-coordinate compounds are also known [1,2]. In contrast five-coordinate copper(I) compounds are unusual, with six-coordinate being unknown for copper(I) [1,2]. The small number of mononuclear five coordinate copper(I) complexes reported to date occur with macrocyclic [3–5] or acyclic [6–8] ligands and the coordination geometry observed with d^{10} metal centers may be a consequence of the geometrical constraints imposed by the nature of these ligands [9] (Scheme 1).

Metal complexes of dipicolinic acid, otherwise known as pyridine-2,6-dicarboxylic acid, have received considerable interest and the number of crystal structure determinations of such complexes exceeds 200 to date. Despite this fact, metal complexes of its esters, which are potentially tridentate ligands, are scarce and only three structures, namely that of Co(II) [10] and Eu(III) [11] complexes of diethyldipicolinate and $[ReBr(CO)_3L]$ (L = methylethyldipicolinate) [12] have been established. The Co(II) complex, which was one of a series of $MLCl_2$ complexes [M = Ni(II), Co(II), Mn(II) and Cu(II)] contains the diethyl ester acting as a tridentate ligand, whereas the methylethyldipicolinate ligand in the rhenium(I) complex acts in a bidentate chelate mode, with the carbonyl groups in a facial arrangement about the distorted octahedral metal center [12]. To the best of our knowledge, there is as yet no known example of a metal complex with dimethyl dipicolinate ligand (I). In the present paper we report on the synthesis and characterization of copper(I) halide, pseudohalide, nitrate and perchlorate complexes of such a dimethyl ester ligand,

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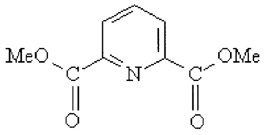

(I)

Scheme 1.

along with X-ray structure determination of the title perchlorate complex, the first to have been reported.

2. Experimental

Dimethyldipicolinate (abbreviated as dmdp) was purchased from Aldrich, other chemicals were of analytical grade quality.

2.1. Preparation of the complexes

2.1.1. Cu(dmdp)X ($X = Cl, Br, I, N_3, NCO$) complexes

The copper(I) halide and pseudohalide complexes were prepared by one or the other of the following general methods.

A stoichiometric amount of an aqueous solution of $CuSO_4 \cdot 5H_2O$ (1.5 g, 6 mmol) was added to an aqueous solution of NaX in the presence of L(+)-ascorbic acid. The precipitated CuX was washed several times with water, then dissolved by slow addition of a calculated quantity of NaX under constant stirring, and filtered. To this filtrate an ethanolic solution of dmdp (1.56 g, 8 mmol) was added and the final mixture allowed to stand in an open beaker until the complexes deposited. In some cases a precipitate was formed upon addition of the ligand. In such cases the mixture was boiled until complete dissolution, and allowed to stand in open air, until the complexes deposited. In the case of the 1:1 cyanato complex, the orange precipitate that was formed upon addition of KNCO solution, should be filtered and dried immediately; addition of excess KNCO dissolves the precipitate.

2.1.2. Cu(dmdp)$_2$X ($X = NO_3$ or ClO_4)

These two complexes were prepared by mixing an aqueous ethanolic solution of $Cu(NO_3)_2 \cdot 3H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$ (4 mmol) and dmdp (9 mmol) followed by addition of L(+)-ascorbic acid. The final mixture was boiled, then cooled and allowed to stand for several days. Good quality crystals of the perchlorate complex were obtained by a very slow evaporation of the solvent.

2.2. Physical measurements

Elemental analysis results and some physical properties of the isolated complexes are listed in Table 1. The IR spectral data for some complexes are given in Table 2. The experimental procedures and instruments used for different physical measurements are as described previously [13].

2.3. X-ray crystallography

$[Cu(dmdp)_2]ClO_4$, $C_{18}H_{18}ClCuN_2O_{12}$, fw = 553.33, triclinic, space group $P\bar{1}$, $a = 10.366(5)$ Å, $b = 10.471(5)$ Å, $c = 11.863(7)$ Å, $\alpha = 113.91(3)°$, $\beta = 109.69(3)°$, $\gamma = 93.62(3)°$, $V = 1078.1(10)$ Å^3, $Z = 2$, $d_{calc} = 1.705$ Mg m^{-3}. The X-ray single crystal data were collected on a modified STOE four circle diffractometer. Crystal size: $0.25 \times 0.20 \times 0.16$ mm. Graphite monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å) with the ω-scan technique was used to collect the data set. The accurate unit cell parameters were determined from automatic centering of 25 reflections ($7.4° < \theta < 14.9°$) and refined by the least-squares method; 4368 reflections (3784 independent reflections, $R_{int} = 0.0330$) were collected in the range $2.86° < \theta < 25.00°$. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2, using the SHELXTL/PC V 5.03 [14] program package. The final R indices are 0.0654 (R_1) and 0.1670 (wR_2) [$I > 2\sigma(I)$]. Goodness of fit on F^2 is 1.053. Number of refined parameters is 311. Maximum and minimum peaks in the final difference Fourier synthesis were 0.880 and −0.732 e Å^{-3}. Selected bond parameters are given in Table 3.

3. Results and discussion

The reaction between copper(I) salts and dmdp or the reduction of the copper(II) ion in the presence of this ligand and NaX afford the complexes given in Table 1. All complexes, except the cyanate, are sufficiently stable against air oxidation when well dried. These complexes are colored and, except the nitrate and perchlorate, insoluble in many polar solvents. In many cases the complexes decompose in H_2O and EtOH giving white turbidity after a few minutes. The perchlorate and nitrate complexes are soluble in polar and non-polar solvents producing conducting solutions with molar conductivities around 98 m^2 Ω^{-1} mol^{-1} in EtOH, indicating their ionic form in such a solvent.

3.1. Structure of the [Cu(dmdp)$_2$]ClO$_4$ complex

Fig. 1 illustrates the principle structural features of the complex and selected bond distances and bond angles are given in Table 3. As can be seen from Figs.

Table 1
Analytical and electronic spectra (nm) data

	Complex	Color	Analysis (found(calculated)(%))					Electronic spectra (nm) [a]
			C	H	N	Cu	X	
1	[Cu(dmdp)]Cl	brown needle like crystals	37.2 (36.7)	3.2 (3.8)	4.9 (4.8)	21.3 (21.6)	12.3 (12.1)	404vs, 488sh, 590sh
2	[Cu(dmdp)]Br	brown needle like crystals	32.1 (31.9)	2.9 (2.7)	4.2 (4.1)	19.2 (18.8)	23.8 (23.6)	404vs, br, 595sh
3	[Cu(dmdp)]I	shiny brown needle like crystals	28.5 (28.0)	2.5 (2.4)	3.5 (3.6)	17.0 (16.5)	33.1 (32.9)	407vs, br, 488sh, 620sh
4	[Cu(dmdp)]N_3	dark brown micro-crystal powder	35.5 (35.9)	3.1 (3.0)	17.7 (18.6)	20.9 (21.1)		500vs, br 656st, br
5	[Cu(dmdp)](OCN)	orange powder	40.2 (39.9)	3.1 (3.0)	9.5 (9.3)	21.4 (21.1)		344s, 440sh
6	$[Cu(dmdp)_2](NO_3)$	brown powder	42.1 (41.6)	3.8 (3.5)	8.2 (8.1)	12.8 (12.2)		500vs, br, 656s, br
7	$[Cu(dmdp)_2](ClO_4)$	brown crystals	39.2 (39.1)	3.4 (3.3)	5.2 (5.1)	11.9 (11.5)		440vs, br, 650s, br

v, very; s, strong; br, broad; sh, shoulder.

[a] Solid samples mulled in Nujol.

Table 2
IR spectral data of dmdp and some complexes (cm^{-1})

Dmdp	3	4	7	Assignment
1749vs		1745w	1744s	
1731s	1731vs	1728s	1727vs	νC=O
1573m	1579s	1570w	1584s	
	1554w	1552w	1554w	
1461m	1485w	1484m		
1458w		1466m		
				pyridine ring vibrations
1438m	1448w	1449m	1449w	
1427w	1428s	1431s	1428s	
		1413m		
1290s	1304s	1292s	1297s	
1245vs	1251vs	1248vs	1250vs	νC–O+$\nu(COO)_{sym}$
1198m	1195m	1195m	1198s	
1166m	1165w	1165m		
				ring C–H
1145m	1143m	1145w		
1081m	1082s	1072w	1085s	
999s	993vs	995vs	984vs	ring breathing
953m	949s	946w	943s	
862w	870s	862w	872m	
852m	842s	838w	847m	ring C–H vibrations
811m	815s	813m	816m	
758s	749s	752s	757vs	
721m	726s	712m	725s	δCOO
697m	692s	689s	695s	
645m	649s	646w	622vs	ring vibrations
	408m	407w	409w	

Abbreviations: s, strong; m, medium; w, weak; v, very.

Table 3
Selected bond lengths (Å) and angles (°) for $[Cu(dmdp)_2]ClO_4$

Bond lengths			
Cu(1)–N(2)	1.957(5)	Cu(1)–N(1)	1.974(5)
Cu(1)–O(3)	2.264(4)	Cu(1)–O(7)	2.318(4)
Cu(1)–O(2)	2.622(5)	Cu(1)–O(5)	2.622(5)
O(1)–C(1)	1.200(8)	O(2)–C(1)	1.329(8)
O(2)–C(8)	1.457(7)	C(1)–C(2)	1.495(5)
C(6)–C(7)	1.492(9)	C(7)–O(3)	1.219(7)
C(7)–O(3)	1.302(7)	O(4)–C(9)	1.455(8)
O(5)–C(10)	1.210(8)	O(6)–C(10)	1.330(8)
O(6)–C(17)	1.441(9)	C(10)–C(11)	1.509(9)
C(15)–C(16)	1.494(9)	C(16)–O(7)	1.207(7)
C(16)–O(8)	1.332(8)	O(8)–C(18)	1.466(8)
Bond angles			
N(2)–Cu(1)–N(1)	148.4(2)	N(2)–Cu(1)–O(3)	120.6(2)
N(1)–Cu(1)–O(3)	78.2(2)	N(2)–Cu(1)–O(7)	78.1(2)
N(1)–Cu(1)–O(7)	125.0(2)	O(3)–Cu(1)–O(7)	103.2(2)
1N(2)–Cu(1)–O(2)	96.2(2)	N(1)–Cu(1)–O(2)	69.8(2)
O(3)–Cu(1)–O(2)	143.2(2)	O(7)–Cu(1)–O(2)	81.7(2)
N(2)–Cu(1)–O(5)	72.9(2)	N(1)–Cu(1)–O(5)	84.0(2)
O(3)–Cu(1)–O(5)	87.2(2)	O(7)–Cu(1)–O(5)	150.5(2)
O(2)–Cu(1)–O(5)	106.8(2)		

1 and 2 the structure consists of a packing of $[Cu(dmdp)_2]^+$ cations and ClO_4^- anions. In the cation, the copper(I) atom links two dmdp molecules differently. Molecule A links the metal center by both carbonyl oxygen atoms of the methyl carboxylate [Cu(1)–O(5) = 2.622(5) Å and Cu(1)–O(7) = 2.318(4) Å] and the nitrogen atom of the pyridine ring [Cu(1)–N(2) = 1.957(5) Å]. Molecule B binds the copper(I) center by the carbonyl oxygen of one methylcarboxylate group and oxygen atom of –COMe of the second methylcarboxylate (with a free C=O group) [Cu(1)–O(3) = 2.264(4) Å and Cu(1)–O(2) = 2.622(5) Å] and the heterocyclic nitrogen atom [Cu(1)–N(1) = 1.974(5) Å]. Thus both ligand molecules are acting in the chelating tridentate mode although they are behaving differently. The copper(I) center has, therefore, a six-coordinate (4+2) environment having a distorted octahedral geometry. The Cu–N distances in the present complex are a little shorter than the corresponding values [2.053(4) and 2.064(5) Å], [2.020(8) and 2.044(9) Å] and 1.995(7) Å found in the structures of $[Cu_2(pyrazinic\ acid)_2I_2]\cdot 3H_2O$ [15], $[Cu(nicotinic\ acid)_2Cl]_n$ [16] and $[Cu(isonicotinic\ acid)Cl]_n$ [17], respectively; where all these acids function as N-monodentate ligands compared with the tridentate chelating dmdp ligand. The Cu–O bonds are larger than those found in $[CuI(isopropylquinaldate)]_2$ [2.33(1) Å], $[CuI(n\text{-butylquinaldate})]_2$ [2.315(4) Å] [18] and $[CuBr(2\text{-benzoylpyridine})]_2$ [2.315(5) Å] [19].

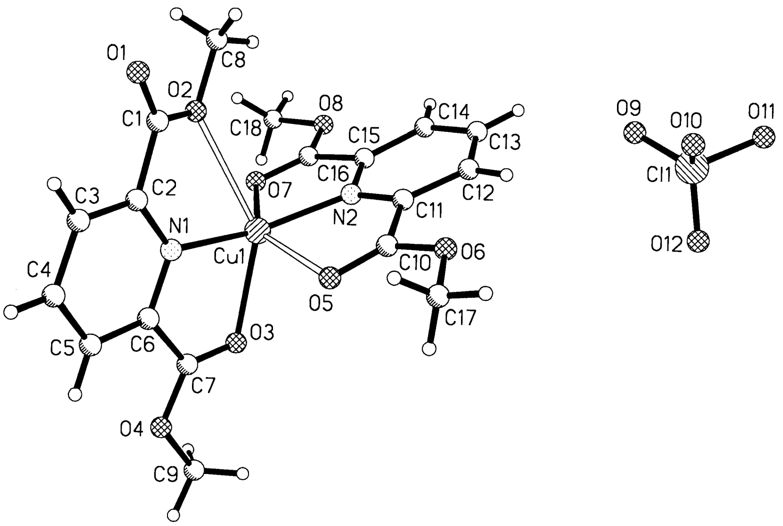

Fig. 1. Molecular structure and atom labeling of the $[Cu(dmdp)_2]ClO_4$ complex.

3.2. Electronic spectra

The electronic spectra (Table 1, Fig. 3) of the solid copper(I) complexes mulled in Nujol exhibit strong absorption bands in the visible region which are due to a metal to ligand charge transfer (MLCT) from Cu(I) d^{10} to an empty π^* orbital of the dmdp ligand. These complexes, however, show two such MLCT bands similar to those that occur in the copper(I) pyrazinic acid complexes [15], the bis-(arylazo)oximates of copper(I) [20,21] and the bis-(2-phenylazo)-pyridine) copper(I) complex [22]. The two bands appear at 700–780 and 550–580 nm, in the latter two cases. In an octahedral environment, the metal valence d orbitals split into two sublevels, e_g and t_{2g}. If the two MLCT bands observed in the spectra of the present complexes are due to e_g–π^* (590–760 nm) and t_2g–π^* (350–490 nm) the energy gap between them lie in the range 11500–9400 cm^{-1}. This difference is much greater than those observed in the case of copper(I) complexes of pyrazinic acid (8500–6200 cm^{-1}) with a tetrahedral copper(I) environment [15]. In the grossly planar and unsaturated macrocyclic environment for copper(I), an allowed transition is documented [23,24] near 700 nm.

3.3. IR spectra

The IR spectra for dmdp and some of its copper(I) complexes are given in Table 2. The spectrum of the free ligand shows a very strong split band with two maxima

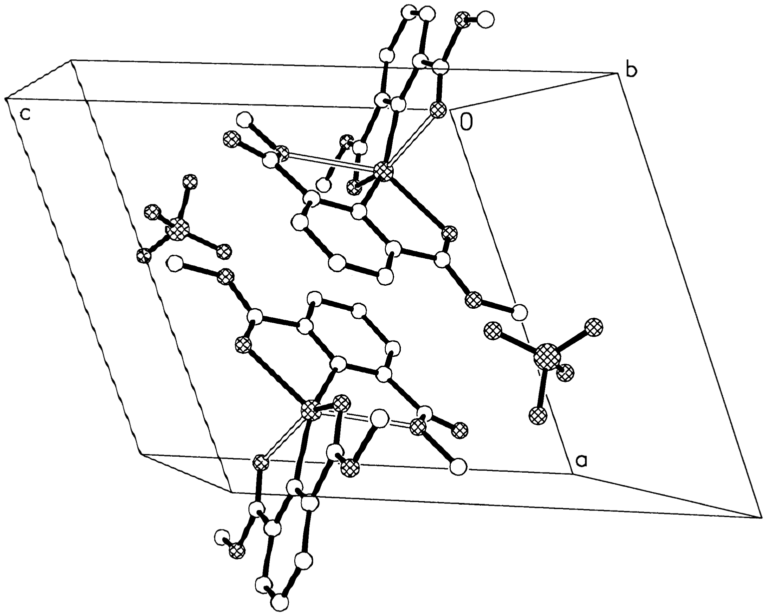

Fig. 2. Cell plot of the $[Cu(dmdp)_2]ClO_4$ complex.

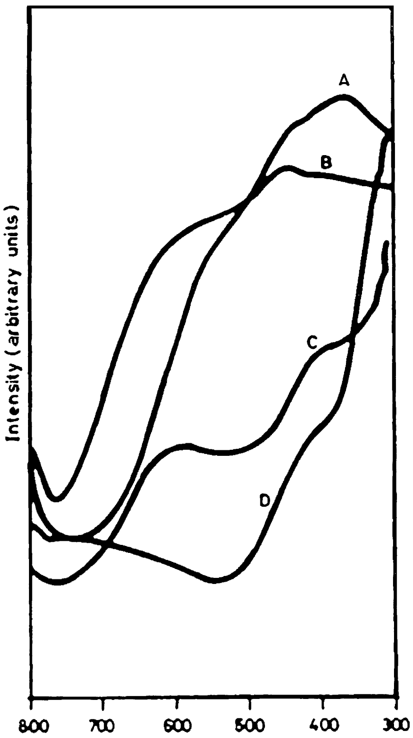

Fig. 3. Electronic spectra of solid complexes (nm): (A) [Cu(dmdp)]Cl; (B) [Cu(dmdp)]N_3; (C) [Cu(dmdp)$_2$]ClO_4; (D) [Cu(dmdp)]OCN.

at 1749 and 1731 cm^{-1} due to the νC=O mode and two bands at 1290 and 1245 cm^{-1} related to the νC–O mode of methyl carboxylate groups. Spectra of all isolated complexes exhibit the corresponding bands around 1740, 1727 and 1300, 1250 cm^{-1}, respectively. Thus the vibration due to νC=O and those due to νC–O are slightly shifted to lower and higher frequencies, respectively, upon complexation of dmdp, suggesting the participation of the two carboxylate groups in bond formation. This behavior resembles that of esters of pyridine monocarboxylic acid in which the carbonyl group is involved in bond formation [25]. The IR spectra, however, could not distinguish between the bonding modes of the methylcarboxylate groups in the two ligand molecules (see Section 3.1), as each of these molecules contains two –CO_2Me groups. The vibrations in the region 1600–400 cm^{-1}, related to the pyridine moiety, are shifted to higher frequencies in the complexes. Thus the two ligand molecules are acting in the bichelating tridentate mode in all isolated complexes. In the spectrum of the 1:1 copper(I) azide complex, two strong maxima at 2094 and 2057 cm^{-1} due to $\nu_{as}(N_3)$ are observed, but no bands could be located in the region 1350–1270 cm^{-1} $\nu_s(N_3)$ due to the ligand vibrations. The appearance of the former bands suggest that the complex contains bridging azido groups; the lower frequency band, which is similar to that of [Cu(Ph_3P)N_3]$_2$ [26], may suggest a symmetrical μ-1,3 azide whereas the band at 2094 cm^{-1} suggests asymmetrical μ-1,3 or μ-1,1 azides [27]. We may assign five-coordinate copper(I) in this azide complex assuming a dimer structure, but a polymeric six-coordinate copper(I) geometry cannot be excluded. The copper(I) cyanato complex showed characteristic asymmetric and symmetric NCO stretching vibrations at 2240 (shoulder), 2224 and 1340, 1300 cm^{-1}, respectively. Such values are at substantially higher frequencies than the free-ion values [28], and this is consistent with a bridging N-cyanate rather than an O-bonded group [29]. Similarly, the halide 1:1 complexes do not show the νCu–X bands in the range 400–200 cm^{-1}, and therefore, such complexes may adopt five- or six-coordinate structures. The spectrum of the 1:2 perchlorate complex exhibits the following bands: 1112 cm^{-1} [broad] (ν3), 624 cm^{-1} (ν4), confirming the ionic nature of the ClO_4 [30] as proved by X-ray crystallography (above section). The nitrate complex showed bands at 1362 and 492 cm^{-1}, a result that is consistent with an ionic nitrate group [30], and therefore, this complex resembles the perchlorate one having a six-coordinate copper(I) geometry.

4. Supplementary data

Further details of the crystal structure investigation are available from the Cambridge Crystallographic Data Centre CCDC No. 194579, The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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