Inorganica Chimica Acta, *171* (1990) 121–125

The Coordination Chemistry of Divalent Cobalt, Nickel and Copper

Part 14. The Characterisation of Copper Complexes with Potentially Bidentate Ligands Having Phosphorus Oxide and Tertiary Amine Donor Groups: a Crystal Structure of Chlorobis(*P*-(*N*,*N*-dimethylaminomethyl)-*P*,*P*-diphenylphosphine oxide)copper(II) Tetrachlorocuprate(II)

JAN G. H. DU PREEZ, BERNARDUS J. A. M. VAN BRECHT* and IRENE WARDEN**

Chemistry Department, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000 (South Africa)

(Received September 12, 1989; revised January 4, 1990)

Abstract

The three ligands *P*-dimethylaminomethyl-*P*-phenylphosphinic acid, dapa, *P*-(*N*,*N*-dimethylaminoethyl)-*P*,*P*-diphenylphosphine oxide, depo, and *P*-(*N*,*N*-dimethylaminomethyl)-*P*,*P*-diphenylphosphine oxide, dmpo, were prepared. Copper complexes were isolated and characterised. The coordination sphere of $Cu(dapa)_2 \cdot H_2O$ was assigned a distorted octahedral symmetry consisting of two amine nitrogen, one water oxygen and three phosphinic acid oxygen atoms, the phosphinic acid group of one dapa ligand being coordinated to two copper atoms. Compound $CuCl_3(H \cdot depo)$ was found to have a distorted tetrahedral chromophore containing the three chlorine and an amine nitrogen as donor atoms. A crystal structure determination was performed on $(CuCl_2)_3(dmpo)_4$; tetragonal, space group $P\bar{4}2_1c$, $a = b = 15.330(2)$, $c = 13.992(4)$ Å, $Z = 2$.

The compound consisted of two penta-coordinate $[Cu(dmpo)_2Cl]^+$ cations and a tetragonally distorted $CuCl_4^{2-}$ anion. The symmetry of the chromophores of the cations was highly distorted square pyramidal, the donor atoms being the phosphine oxide oxygen and amine nitrogen from each of two dmpo ligands and the chlorine atom. An analogous structure was assigned to $(CuBr_2)_3(dmpo)_4$.

Introduction

In these laboratories we are engaged in a search for solvent extractants suitable for the concentration and separation of divalent cobalt, nickel and copper [1]. A particularly vexing problem is the removal of small quantities of cobalt present in some nickel concentrates. Bis(2-ethylhexyl)phosphoric acid, HDEHP, is well known for its cobalt specific properties and has been the subject of many investigations [2], but is not ideally suited for this task. Other alkyl substituted phosphoric and phosphonic acids have recently been investigated [3]. With this in mind, three potentially bidentate ligands, *P*-dimethylaminomethyl-*P*-phenylphosphinic acid, dapa, *P*-(*N*,*N*-dimethylaminoethyl)-*P*,*P*-diphenylphosphine oxide, depo, and *P*-(*N*,*N*-dimethylaminomethyl)-*P*,*P*-diphenylphosphine oxide, dmpo were prepared. These ligands can readily be converted into solvent extractants by exchanging the methyl groups for long alkyl chains. Numerous metal complexes were prepared in order to establish if there were significant differences in coordination properties of these ligands with respect to cobalt, nickel and copper. The results of the investigation pertaining to the cobalt and nickel complexes of depo and dmpo have already been reported [4]. In this paper the preparation and characterisation of the copper complexes of all three ligands will be discussed.

Experimental

Preparations

Benzenephosphinic acid (28.4 g) was dissolved in sodium dried freshly distilled tetrahydrofuran under a nitrogen atmosphere. Excess *N*,*N*,*N*′,*N*′-tetramethyldiaminomethane was added dropwise to the solution at 40 °C. The reaction mixture was then gently heated to reflux for 24 h resulting in a white hygroscopic precipitate of *P*-(*N*,*N*-dimethylaminomethyl)-*P*-phenylphosphinic acid. The precipitate was recrystallised from a mixture of ethanol and ether (yield 50%, melting point 207–208 °C).

The ligands *P*-(*N*,*N*-dimethylaminomethyl)-*P*,*P*-diphenylphosphine oxide and *P*-(*N*,*N*-dimethylaminoethyl)-*P*,*P*-diphenylphosphine oxide were prepared as previously described [4].

The sodium salt of dapa (9.5 mmol) dissolved in a hot mixture of methyl cyanide (15 cm^3), butanol

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*Author to whom correspondence should be addressed.

**Permanent address: The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QY, U.K.

0020-1693/90/$3.50

(15 cm^3) and ethanol (15 cm^3) was added dropwise to a hot solution of $CuCl_2 \cdot 3H_2O$ (2 mmol) in butanol (10 cm^3). The resultant sodium chloride was removed by centrifuging the hot solution. Dark blue crystals were obtained on cooling. These were dried under vacuum at 100 °C for 1 h yielding Cu(dapa)$_2 \cdot H_2O$ (yield 50%).

Hot solutions of hydrochloric acid (2 mmol) in ethanol (5 cm^3), copper chloride (2 mmol) in butanol (15 cm^3) and depo (2.1 mmol) in butanol (10 cm^3) were added together. Slow cooling to -15 °C afforded yellow crystals of $CuCl_3$(H·depo) (yield 84%).

A hot solution of dmpo (4.2 mmol) in methyl cyanide (15 cm^3) was added dropwise to a hot clear solution of anhydrous copper chloride (2 mmol) in methyl cyanide (25 cm^3). The addition of ethyl acetate (15 cm^3) resulted in yellow crystals of $(CuCl_2)_3$(dmpo)$_4$ (yield 30%). Black crystals of $(CuBr_2)_3$(dmpo)$_4$ were obtained in an analogous manner, but without the addition of ethyl acetate (yield 70%).

Analysis and Characterisation

The analytical and characterisation procedures as well as the apparatus used were the same as those previously described [4].

Structure Determination of [Cu(dmpo)Cl]$_2$[CuCl$_4$]

Crystal data

$(C_{30}H_{36}ClN_2O_2P_2Cu)_2^+(CuCl_4)^{2-}$, $M = 1440.5$, tetragonal, space group $P\bar{4}2_1c$, $a = b = 15.330(2)$, $c = 13.992(4)$ Å, $U = 3288.(1)$ Å^3, $Z = 2$, $D_m = 1.42$, $D_c = 1.45$ g/cm^3, $F(000) = 1482$, μ(Mo Kα) = 12.8 cm^{-1}, $\lambda = 0.7107$ Å.

Weissenberg photographs were used to determine the space group. Crystallographic data was collected as previously described [5]. The intensities of 1713 observed reflections in the range $3° < \theta < 25°$ were measured. Lorentz–polarization and empirical absorption corrections were performed [6]. The structure was solved by Patterson and Fourier techniques. All atoms except hydrogen atoms were refined anisotropically. Restrictions were placed on the anisotropic parameters of the copper and chlorine atoms in special positions. The phenyl and methyl hydrogen atoms were placed at theoretically calculated positions with respect to the adjacent carbon atom. The methyl and methylene hydrogen atoms were refined with a common temperature factor. The same procedure was followed with the phenyl hydrogen atoms. The final refinement was done using 1310 unique reflections having $I > 2\sigma(I)$ and omitting the 222 reflection. This led to convergence with $R = 0.0571$ and $R_w = 0.0437$ where $\omega \propto 1/\sigma^2$. The final difference map contained no peak of height greater than 0.6 e Å^{-3}. All calculations were performed with SHELX 76 and PARST programs [7]. The figure was prepared using the program PLUTO. See also 'Supplementary Material' and Table 3.

After numerous unsuccessful attempts, using a variety of different methods, the complex Cu(dapa)$_2 \cdot H_2O$ was isolated although not in a very pure form, Table 1. The presence of a single water molecule was confirmed by thermogravimetric analysis. Like its cogeners Co(dapa)$_2 \cdot H_2O$ and Ni(dapa)$_2 \cdot H_2O$ [8], this compound is almost insoluble, making purification by recrystallisation impossible. The low solubility is an indication of bridging in the compound, the formula units being linked by covalent bonds. There are numerous instances where phosphonate and phosphinite behave as bidentate groups which results in such insoluble, bridged compounds [9]. The phosphinite group is similar to acetate. It is interesting to note that dapa is an amino acid resembling glycine and that M(glycine)$_2 \cdot H_2O$ complexes (M = Co, Ni and Cu) having low solubility have also been isolated. The infrared spectra of both monodentate and bidentate acetate is well understood [10]. The infrared spectra of phosphinite can be interpreted in an analogous manner. The $\nu(POO)_s$ and $\nu(POO)_a$ bands in the infrared spectrum of Cu(dapa)$_2 \cdot H_2O$ are both split and shifted to lower energy when compared to the infrared bands of dapa. This indicates that both phosphinite groups are coordinated, one in a monodentate and the second in a bidentate manner. The low solubility can be rationalised if the two oxygen atoms of the bidentate phosphinite group are coordinated to different

TABLE 1. Analytical and conductivity data with calculated values in parentheses

Complex	Analytical (%)					Conductivity^a (S cm^2/mol)	
	M	Anion	C	H	N		
						Λ_{500}	Λ_{1000}
Cu(dapa)$_2 \cdot H_2O$	13.1(13.2)		45.8(45.3)	5.7(5.9)	6.2(5.9)	0.3	0.3
$CuCl_3$(H·depo)	14.3(14.3)	23.8(23.9)	43.3(43.3)	4.8(4.8)	3.2(3.2)	64.1	74.7
$(CuCl_2)_3$(dmpo)$_4$	13.2(13.2)	14.4(14.8)	49.8(50.0)	5.0(5.0)	3.9(3.9)	22.7	24.1
$(CuBr_2)_3$(dmpo)$_4$	11.4(11.1)	27.3(27.8)	42.7(42.2)	4.3(4.3)	3.3(3.3)	71.0	77.9

$^a\Lambda_{500}$ and Λ_{1000} molar conductivity of 0.002 and 0.001 mol/dm^3 solutions.

TABLE 2. Selected bands in the infrared and electronic spectra with extinction coefficients in parentheses

Complex	Medium	Infrared (cm^{-1})	Electronic (cm^{-1})
Cu(dapa)$_2$·H$_2$O	solid	405, 467, 482, 1008, 1022, 1040, 1175, 1195	14925
	butanol-1		15152(218)
H·dapa	solid	505, 1050, 1190	
CuCl$_3$(H·depo)	solid	300, 450, 1165	8510, 22730, 26040
	CH$_3$NO$_2$		8700(61), 10900(92)
depo	solid	1170–1180	
(CuCl$_2$)$_3$(dmpo)$_4$	solid	240–265, 465–470, 1160–1100	9350, 11770, 13790
	CH$_3$NO$_2$		11765(123)
(CuBr$_2$)$_3$(dmpo)$_4$	solid	470, 1140	5130(w), 9000, 12010, 17040(sh), 18420
	CH$_3$NO$_2$		11830(124), 12270(123)
dmpo	solid	1170	

w = weak; sh = shoulder.

copper atoms thus forming a chain. The region 470 to 500 cm^{-1}, where the ν(Cu–O) skeletal vibrations are expected, contains three bands which agree with the above assignment. There is a further band at 405 cm^{-1} which may be assigned to the ν(Cu–N) vibration, thus indicating coordination of the amine group. The solid reflectance electronic spectrum consists of a single band at 14925 cm^{-1}, Table 2, which is indicative of an octahedral coordination sphere. The solution spectrum, which may be used to confirm this, cannot be obtained since bridging is destroyed in solution. An octahedral chromophore can be achieved if the sixth coordination site is occupied by the oxygen atom from the water molecule. Thermogravimetric analysis indicates that the water molecule is tightly bound and it is only released at 290 °C. The assignment to Cu(dapa)$_2$·H$_2$O of bridged octahedral chromophores, similar to those of Cu(glycine)$_2$·H$_2$O, can only be confirmed by single crystal X-ray crystallography. However, crystals suitable for this technique could not be found.

The analytical data confirmed the isolation of the CuCl$_3$(H·depo) complex. Its preparation differs from that of CoCl$_3$(H·depo) in that it is isolated from a solution containing anhydrous copper chloride, depo and hydrochloric acid while the cobalt complex can be obtained directly by reacting equimolar amounts of anhydrous cobalt chloride and depo; the source of protons in the latter preparation is from a tautomerisation reaction involving the ligand [4]. The reason for this difference could not be ascertained. The characterisation data from the copper complex was not interpreted in the same manner as the data from the cobalt complex. The relatively low energies of the bands in the electronic spectra of both the solution and the solid complex, Table 2, is indicative of copper in a tetrahedral coordination sphere. Furthermore, since the spectrum of solid CuCl$_3$(H·depo) has a shoulder at 8700 cm^{-1} on the main band at 10 900 cm^{-1}, considerable distortion in the symmetry of the chromophore is anticipated. The most likely explanation is a coordination sphere consisting of three Cl atoms and one donor atom from depo. The infrared spectrum has an intense band at 300 cm^{-1} which is assigned to the ν(Cu–Cl) vibration and therefore indicates coordination of some of the chlorine atoms. The ligand depo can bond either through the amine nitrogen or the phosphine oxide group. Coordination of the nitrogen is usually shown by the presence of a ν(Cu–N) skeletal vibration in the 400–500 cm^{-1} region of the infrared spectrum. Since uncoordinated depo has three bands in this region identification of the skeletal vibration is difficult. Coordination of a phosphine oxide group results in a shift to lower energy of the ν(P=O) band. Such a shift was indeed observed. However, a similar shift will occur when this group becomes protonated. If the amine nitrogen atom is coordinated to the copper, the phosphine oxide will most likely be protonated and vice versa. Protonation of the amine is readily observed by a broad band at 2500 cm^{-1} in the infrared spectrum. Since this band is not evident, the coordination sphere is thought to consist of three chlorine atoms and a nitrogen atom. The monodentate behaviour of depo can be attributed both to steric reasons and to the inherent instability of a six-membered chelate.

The complexes (CuX$_2$)$_3$(dmpo)$_4$ (X = Cl, Br) were isolated in pure crystalline form. The empirical formulae coincide with those of the (MX$_2$)$_3$(dmpo)$_4$ (M = Co, Ni) complexes previously reported [4]. These complexes were shown to consist of pentacoordinate cations MX(dmpa)$_2$$^+$ and tetrahedral

TABLE 3. Fractional atomic coordinates (X10^4) for non-hydrogen atoms with e.s.d.s in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu 1	0	0	5000
Cu 2	0	5000	−174(1)
Cl 1	1076(2)	779(2)	5684(2)
Cl 2	0	5000	1518(2)
O 1	−12(4)	3720(3)	−631(4)
P 1	−889(2)	3291(2)	−512(2)
N 1	−1303(4)	4993(6)	−332(5)
C 11	−1777(6)	5682(6)	232(8)
C 12	−1522(6)	5155(8)	−1421(5)
C 1	−1621(6)	4091(7)	−15(8)
C 21	−855(6)	2409(6)	312(6)
C 22	−336(7)	2480(7)	1121(7)
C 23	−256(8)	1811(8)	1741(8)
C 24	−695(8)	1055(8)	1603(8)
C 25	−1215(8)	958(7)	821(8)
C 26	−1308(6)	1636(6)	191(8)
C 31	−1279(6)	2840(6)	−1605(7)
C 32	−678(7)	2464(7)	−2199(7)
C 33	−942(8)	2015(6)	−3031(8)
C 34	−1812(9)	1961(8)	−3228(9)
C 35	−2395(8)	2334(7)	−2638(10)
C 36	−2154(7)	2764(8)	−1839(9)

TABLE 4. Selected interatomic distances (Å) and angles (°) with e.s.d.s in parentheses. Atoms with the suffix A or B are symmetry related to the corresponding atom without the suffix

Cu 1–Cl 1	2.250(3)	Cl 1–Cu 1–Cl 1A	129.7(0)
Cu 2–Cl 2	2.367(4)	Cl 1–Cu 1–Cl 1B	100.4(0)
Cu 2–O 1	2.064(5)	Cl 2–Cu 2–N 1	96.3(2)
Cu 2–N 1	2.010(6)	Cl 2–Cu 2–O 1	108.1(2)
O 1–P 1	1.506(7)	O 1–Cu 2–N 1A	88.9(3)
P 1–C 1	1.803(10)	N 1–Cu 2–O 1	87.3(3)
N 1–C 1	1.531(12)	O 1–Cu 2–O 1A	143.9(2)
N 1–C 11	1.504(11)	N 1–Cu 2–N 1A	167.4(3)
N 1–C 12	1.580(10)	Cu 2–O 1–P 1	112.9(3)
		O 1–P 1–C 1	107.5(4)
		Cu 2–N 1–C 1	106.8(5)
		Cu 2–N 1–C 11	114.7(5)
		Cu 2–N 1–C 12	108.5(4)
		C 1–N 1–C 11	109.2(7)
		C 1–N 1–C 12	110.7(7)
		C 11–N 1–C 12	107.0(7)
		P 1–C 1–N 1	107.7(6)

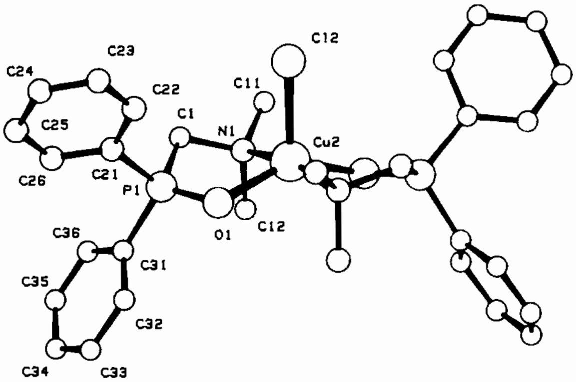

Fig. 1. A perspective view and atomic numbering scheme of the cation $CuCl(dmpo)_2^+$.

MX_4^{2-} anions. This assignment was based almost solely on gaussian analyses of their electronic spectra. The electronic spectra of the two copper complexes are relatively featureless and are unsuitable for diagnostic purposes. A further complication arises in that the CuX_4^{2-} moiety may be either tetrahedral or square planar; the two chromophores having different spectra. Since the evidence for an assignment was limited, a single crystal X-ray analysis was performed on $(CuCl_2)_3(dmpo)_4$ to determine its structure unequivocally and at the same time corroborate the assignment made for the cobalt and nickel complexes.

The X-ray analysis confirmed the structure to be $[CuCl(dmpo)_2]_2[CuCl_4]$. Fractional atomic coordinates are listed in Table 3. Selected bond distances and angles are given in Table 4 while the cation $CuCl(dmpo)_2^+$ and its atomic numbering is portrayed in Fig. 1. The tetragonal $P\bar{4}2_1c$ space group requires high symmetry within the structure. The Cu 1 atom of the anion $CuCl_4^{2-}$ is in a special position coinciding with a fourfold improper rotation axis. The four Cl 1 atoms of the anion are therefore in equivalent positions. As a result the anion has a tetragonally distorted tetrahedral symmetry, the structure being somewhat flattened. The symmetry of a tetrahedron with a high degree of tetragonal distortion may be described as distorted square planar. The degree of distortion in a tetrahedron can be expressed quantitatively in terms of a parameter *D* [11]. The value of *D* for this anion is 0.232 which is at the lower end of the range reported in literature [11] thus indicating that the distortion is relatively minor. Both Cu 2 and Cl 2 atoms of the cation $CuCl(dmpo)_2^+$ are in special positions. The line containing these two atoms is a twofold axis about which the dmpo ligands may be rotated. The symmetry of the coordination sphere approximates a square pyramid. The basal plane is formed by the O 1 and N 1 atoms of each of the two dmpo ligands, the N 1 atoms being 0.255(7) Å above the plane while the O 1 atoms are displaced 0.164(6) Å below it. Therefore the atoms deviate significantly from planarity. As in most square pyramidal structures the metal atom lies above the basal plane, the displacement for this compound being 0.476(2) Å. The fact that the tertiary amine nitrogen atoms, N 1, are coordinated to the copper atom and that further restrictions are placed on the orientation of the N 1 atoms by the carbon atoms linking it to the phosphine oxide groups, necessitates a short copper–

carbon distance for one of the associated methyl groups. The Cu 2–C 12 distance is 2.923 Å. This is significantly less than the sum of the van der Waal's radii for copper and the methyl group [12]. The presence of methyl groups fixed in these positions prevents the occupation of the sixth coordination site by a donor atom and results in a five-coordinate cation.

The characterisation data of solid $[CuCl(dmpo)_2]_2[CuCl_4]$ can readily be interpreted once the crystal structure is known. The infrared spectrum of this compound contains evidence for coordination of the phosphine oxide and amine nitrogen atoms as well as a broad band at 270–240 cm^{-1}. This band is due to overlapping ν(Cu–Cl) bands produced by the anion and cation chromophores; $CuCl_4^{2-}$ has bands at 267 and 248 cm^{-1} [13]. The solid reflectance electronic spectrum consists of a series of overlapping bands in the region 14 000–9000 cm^{-1}. The spectrum of $CuCl_4^{2-}$ consists of a single band at 9000 cm^{-1} while penta-coordinate complexes having oxygen, nitrogen and chlorine donor atoms have bands above 10 000 cm^{-1} [14]. The interpretation of the characterisation data from solutions of $[CuCl(dmpo)_2]_2[CuCl_4]$ is different. The low conductivity data, Table 1, of the complex dissolved in nitromethane indicates few ions in solution. The electronic spectrum of the complex consists of a single band at 11 765 cm^{-1}. Therefore, the predominant species in solution cannot be the $CuCl(dmpo)_2^+$ and $CuCl_4^{2-}$. The driving force for the formation of $[CuCl(dmpo)_2]_2[CuCl_4]$ from solutions having low concentrations of the constituent ions, is probably the lattice energy produced by the large doubly charged anions combining with the large cations.

The corresponding copper bromide complex was tentatively assigned an analogous $[CuBr(dmpo)_2]_2[CuBr_4]$ structure. This assignment was based on the similarity between the characterisation data of this complex compared to that of the above copper chloride complex. The solid reflectance electronic spectrum can be divided into four regions viz. a weak band at 5130 cm^{-1}, a broad structure stretching from 6000 to 14 500 cm^{-1} with ill-defined maxima at approximately 9000 and 12 010 cm^{-1}, a more intense band at 18 400 cm^{-1} with a shoulder at 17 040 cm^{-1} and very intense band starting at 20 800 cm^{-1}; the last region being ascribed to charge transfer transitions. The $CuBr_4$ chromophore is known to exhibit a very weak band at approximately 5000 cm^{-1} and a more intense band at about 8000 cm^{-1} [15]. Both these features could be identified in the above spectrum. The band at 18 400 cm^{-1} is at considerably higher energy than for the corresponding copper chloride complex. This is ascribed to the different steric and weaker donor properties of the bromide when compared to that of chloride. This is in agreement with the greater conductivity values obtained for the bromide complex Table 1; nitromethane can displace a bromide ion from the coordination sphere of copper more easily than a chloride ion.

Supplementary Material

A complete list of bond distances and angles, thermal parameters, hydrogen atom positions and structure factor tables may be obtained from the author.

Acknowledgements

The authors wish to acknowledge the financial assistance received from the South African Council for Scientific and Industrial Research, and the University of Port Elizabeth. We also thank the C.S.I.R. for the services of the National X-ray Data Collecting Facility in providing the diffractometer data.

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