Contribution from the Inorganic Chemistry Research Laboratory, University of Port Elizabeth, Port Elizabeth, South Africa

The Co-ordination Chemistry of Divalent Cobalt, Nickel and Copper. Part I. Five-coordinate Copper(II) Complexes with New Thiodiacetamide Ligands

L. Ackerman, J.G.H. du Preez, and M.L. Gibson

Received February 20, 1971

Preparation and properties of new penta-coordinate copper(II) complexes using ligands with OSO sets of donor atoms, viz. N,N,N',N'–tetramethylthiodiacetamide (TTDA) and N,N'–dimethyl–N,N'–diphenylthiodiacetamide (DTDA), are reported. Spectral and conductivity data show that CuX_2L ($X=Cl^-$, Br^-, NO_3^-; L=TTDA and DTDA) are penta-coordinate in both the solid state and solution. These are compared with copper(II) complexes prepared by using other similar tridentate ligands. Spectral data and X-ray structural analysis (reported earlier) indicated a slightly distorted square pyramidal structure for $CuCl_2$. TTDA.

Introduction

Interest in high spin penta-coordinate complexes of divalent 3d transition metals, has increased considerably in the last few years as indicated by review articles by Sacconi[1] and Ciampolini.[2] These complexes can be stabilized by neutral, potentially tridentate ligands. Such ligands with NNN,[3,4,5] SNN,[6] NSN,[7] ONN,[8] NON,[9] and SNS[10] donor sets, have been used to prepare and study penta-coordinate complexes. This work was undertaken in an endeavour to prepare the first tridentate ligands with OSO sets of donor atoms, for the purpose of isolating and studying their, four-, five- and six-coordinate complexes of divalent cobalt, nickel and copper, and to compare these with those of related ligands. N,N,N',N'–tetramethylthiodiacetamide (TTDA) and N,N'–dimethyl–N,N'–diphenylthiodiacetamide (DTDA) (Figure 1, A) were therefore prepared as well as the various copper(II) complexes, *viz.* CuX_2. L ($X=Cl^-$, Br^-, and NO_3^-) and $Cu(ClO_4)_2$. 2L (L=TTDA and DTDA) and $Cu(BF_4)_2$. 2TTDA.

These compounds were compared with some other newly isolated copper(II) complexes of N,N,N',N'–tetramethyldiglycollamide (TDGA), 3,3'–thiodipropionitrile (TDPN) and 3,3'–iminodipropionitrile (IDPN), *viz.* $CuCl_2$. L (L=TDGA and TDPN), and $CuCl_2$. 2IDPN.

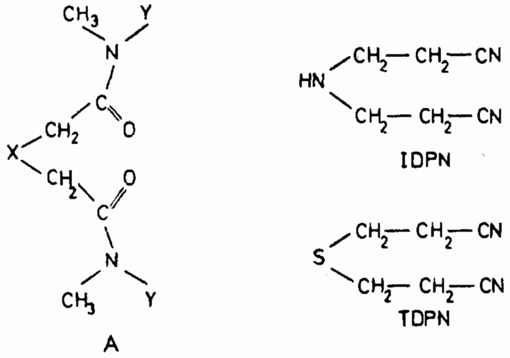

Figure 1. Structural formulae of new ligands.

TTDA when X=S, $Y=CH_3$
DTDA when X=S, $Y=C_6H_5$
TDGA when X=O, $Y=CH_3$

Experimental Section

N,N,N',N'–Tetramethylthiodiacetamide was prepared by refluxing 2,2'–thiodiacetic acid (15 g) in thionyl chloride for five hours, distilling off the solvent and vacuum distilling the crude acid chloride, cutting the fraction boiling at 100-105° (0.5 torr). The orange product was slowly run into a cooled ethereal solution (125 ml) containing a large excess of anhydrous N,N–dimethylamine (175 ml). After completion of the reaction, the dimethylammonium chloride was filtered off, the excess N,N–dimethylamine and ether distilled off and the crude product vacuum distilled cutting the fraction boiling at 168-172° (0.06 torr). A yellow-brown, extremely hygroscopic solid (m.p. 60°C) was obtained (overall yield 40%). (Found: C, 46.3; H, 8.0; N, 13.5. Calculated for TTDA: C, 47.06; H, 7.84; N, 13.73%) N,N'–Dimethyl–N,N'–diphenylthiodiacetamide was prepared similarly to TTDA using N–methylaniline instead of dimethylamine. The crude product dissolved in $CHCl_3$, was washed first with dilute hydrochloric acid (three ti-

---

(1) L. Sacconi, *Pure and Applied Chemistry, 17*, 95 (1968).
(2) M. Ciampolini, *Structure and Bonding, 6*, 52 (1969).
(3) L. Sacconi, I. Bertini, and R. Morassi, *Inorg. Chim.*, 6, 1548, (1967).
(4) Z. Dori and H.B. Gray, *Inorg. Chem.*, 7, 889 (1968).
(5) L. Sacconi, R. Morassi, and S. Midollini, *J. Chem. Soc. (A)*, 1510 (1968), and references therein.
(6) L. Sacconi and G.P. Speroni, *Inorg. Chem.*, 7, 295 (1968).
(7) M. Ciampolini and J. Gelsomini, *Inorg. Chem.*, 6, 1821 (1967).
(8) L. Sacconi and I. Bertini, *Inorg. Chem.*, 7, 1178 (1968).
(9) M. Ciampolini and N. Nardi, *Inorg. Chem.* 5, 445 (1967).
(10) S.E. Livingstone and J.D. Nolan, *Aust. J. Chem.*, 22, 1817 (1969).

mes) and finally with aqueous sodium carbonate solution. After drying with anhydrous sodium sulphate and concentrating the $CHCl_3$ solution, crystallization of white DTDA (m.p. 105°) was induced by addition of petroleum ether (overall yield 42%). (Found: C, 65.2; H, 6.2; N, 8.3. Calculated for DTDA: C, 65.85; H, 6.10; N, 8.54%.)

N,N,N′,N′–Tetramethyldiglycollamide was prepared similarly to TTDA, using diglycollic acid as starting material. The crude product was vacuum fractionated between 175-180° (0.8 torr). (Found: C, 50.2; H, 8.7; N, 14.5. Calculated for TDGA: C, 51.06; H, 8.51; N, 14.89%.)

3,3′–Thiodipropionitrile (pure) was obtained from Fluka. 3,3′–Iminodipropionitrile and di–(2–cyanoethyl)ether were obtained from Eastman Organic Chemicals and May and Baker, respectively.

Complexes. All complexes were first washed with ethyl acetate, then ether and dried *in vacuo.*

(a) *Chloro and Bromo Complexes.* Methyl cyanide solutions of TTDA and IDPN as well as methylene dichloride solutions of DTDA and TDGA, were each added in excess to methyl cyanide solutions of anhydrous copper halide. The following complexes crystallised upon standing: Bright-green, non-hygroscopic $CuCl_2 . TTDA$ (Found: Cu, 18.5; Cl, 20.8; C, 28.3; H, 4.7; N, 8.2. Calcd: Cu, 18.74; Cl, 20.98; C, 28.5; H, 4.78; N, 8.30%.) Red-brown, non-hygroscopic $CuBr_2 . TTDA$ (Found: Cu, 13.5; N, 6.0. Calcd. Cu, 13.70; N, 6.04%). (This compound decomposes slowly to CuBr upon standing.) Red-brown, non-hygroscopic $CuBr_2 . DTDA$ (Found: Cu, 11.5; C, 38.8; H, 3.5; N, 5.0. Calcd: Cu, 11.53; C, 39.18; H, 3.63; N, 5.1%). Mauve non-hygroscopic $CuCl_2 . 2IDPN$ (Found: Cu, 16.3; Cl, 18.9; C, 37.6; N, 21.8. Calcd: Cu, 16.7; Cl, 18.66; C, 37.84; N, 22.07%). Efforts to isolate a pure $CuCl_2$ complex of DCE from methyl cyanide solutions, were unsuccessful.

The following complexes were precipitated by ether: bright-green, slightly hygroscopic $CuCl_2 . DTDA$ (Found: C, 46.5; H, 4.3; N, 5.9. Calcd: C, 46.70; H, 4.32; N, 6.05%), and greenish-yellow, very hygroscopic, impure $CuCl_2 . TDGA$. Green, hygroscopic $CuCl_2 . TDPN$ (Found: Cu, 22.7; Cl, 25.7; N, 10.2; C, 26.6; H, 2.8. Calcd: Cu, 23.15; Cl, 25.86; N, 10,20; C, 26.22; H, 2.9%), was prepared by adding excess ligand to an alcoholic solution of anhydrous $CuCl_2$ and precipitating a green oil which produced crystals upon standing.

(b) *Nitrato Complexes.* To a hydrated copper nitrate solution in a 3:2 mixture of methyl cyanide and dimethoxy propane, was added excess ligand either in methyl cyanide (TTDA) or methylene dichloride (DTDA). Blue-green, slightly hygroscopic $Cu(NO_3)_2 . TTDA$ (Found: Cu, 16.4; C, 24.3; H, 4.2; N, 14.1. Calcd: Cu, 16.23; C, 24.52; H, 4.09; N, 14.3%) crystallized from the green oil which separated from the above solution upon addition of ether. Blue-green, slightly hygroscopic $Cu(NO_3)_2 . DTDA$ (Found: Cu, 12.6; C, 40.7; H, 4.0; N, 10.5. Calcd: Cu, 12.33; C, 41.9; H, 3.88; N, 10.86%) crystallised similarly to the above upon addition of petroleum ether.

(c) *Perchlorate and Tetrafluoroborate Complexes.* Excess ligand was added to the hydrated copper salt dissolved in a 2:1 alcohol/dimethoxy propane mixture. Pale-green $Cu(ClO_4)_2 . 2TTDA$ (Found: Cu, 9,5; ClO_4, 29.5; C, 28.3; H, 4.9. Calcd: Cu, 9.47; ClO_4, 29.68; C, 28.63; H, 4.7%), pale-green $Cu(ClO_4)_2 . 2DTDA$ (Found: C, 46.6; H, 4.3; N, 6.0. Calcd: C, 47.03; H, 4.35; N, 6.1%) and pale-green $Cu(BF_4)_2 . 2TTDA$ (Found: C, 29.5; H, 4.8; N, 8.6. Calcd: C, 29.76; H, 4.96; N, 8.68%) crystallized out immediately.

Analysis. Chloride and bromide were determined potentiometrically. Nitrogen was determined by the Kjeldahl method and copper gravimetrically.^{11} Nitrate^{11a} and perchlorate^{12} were done gravimetrically. Organic micro analyses were done at the University of Cape Town. Infrared spectra were run on a Perkin-Elmer 457 spectrophotometer using the KBr disc method. Both the solution and solid reflectance ultraviolet spectra were determined by using a Beckman DK-2A spectrophotometer. Conductivity measurements were done on methyl cyanide solutions using a Metrohm Konduktoskop. Magnetic susceptibility was done by using a Gouy instrument of similar design to a previously described instrument.^{13} $HgCo(CNS)_4$ and $Ni(en)_3S_2O_3$ were used as calibrants.^{14} Diamagnetic corrections were estimated from Pascal's constants.^{14a} Magnetic moments were calculated as previously described.^{15} Temperature independent paramagnetic corrections were not made.

Results and Discussion

Conductivity and Infrared Data. The conductivities of 0.001 *M* solutions for each of the complexes in methyl cyanide, are represented in Table I. Generally speaking, these conductivities increase in the direction chloride, bromide, nitrate, which is the order usually found for complexes of the divalent 3d transition elements. The tetrafluoroborate and perchlorate complexes have different stoichiometries and conductivities which approximately correspond to those of 2:1 electrolytes.

All the complexes revealed a lowering in the carbonyl stretch frequencies of the amide ligands as compared to those of the free ligands. In addition to this, definite splittings occur in those of the chloro and bromo complexes of TTDA and DTDA (Table I). This indication of different $Cu–O_1$, and $Cu–O_2$ distances is in agreement with the values of 2.03 Å and 2.28 Å found in $CuCl_2 . TTDA$ (Figure 3).^{16} Infrared data cannot readily be used to show whether sulphur atoms of thio ether ligands co-ordinate to divalent 3d transition metals.^{17} This is mainly due to: (i) the weak interaction of such sulphur atoms with the metal ions, and (ii) the low intensities of modes in-

---

(11) A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, 3rd Edition. Longmans, London (1961), p. 496.
(a) ibid., p. 583.

(12) Willard and Smith, *Ind. Eng. Chem. Analyt., 11,* 186, 305 (1939).

(13) D. Brown and R. Colton, *J. Chem. Soc.,* 714 (1964).

(14) B.N. Figgis and J. Lewis, Technique of Inorganic Chemistry, IV, 231. (a) ibid., *IV*, 142.

(15) J. Lewis and R.G. Wilkins, Modern Coordination Chemistry, Interscience Publishers Ltd., London (1960), p. 416.

(16) *Acta Cyst.* (1970) *B26,* 1414.

(17) G.W.A. Fowles, R.A. Hoodless, and R.A. Walton, *J. Chem. Soc.*, 5873, (1963).

Talbe I. Physical Data of Copper(II) Complexes.

	M.p., °C	Conductivity (mho cm^2) of 0.001*M* CH_3CN solution at 25°C	I.r. Data $\Delta\nu C{=}O$ cm^{-1}	Magnetic data t, °C	μ_{eff}(B.M.)
$CuCl_2$. TTDA	150	26.0	— 7, —33 [a]	22	1.88
$CuCl_2$. DTDA	144	41.8	—27, —53 [a]	21	1.83
$CuBr_2$. TTDA	149	66.3	— 7, —33 [a]	—	—
$CuBr_2$. DTDA	139	62.9	—30, —53 [a]	21	1.77
$Cu(NO_3)_2$. TTDA	142	85.4	—30	—	—
$Cu(NO_3)_2$. DTDA	124	48.7	—55	22	1.82
$Cu(ClO_4)_2$. 2TTDA	150(d)	328	—27	25	1.71
$Cu(ClO_4)_2$. 2DTDA	150(d)	288	—54	25	1.69
$Cu(BF_4)_2$. 2TTDA	160(d)	203	—30	—	—
$CuCl_2$. TDPN	151	32.9	—	22	1.81
$CuCl_2$. 2IDPN	133	59.6	—	22	1.72
TTDA	60	—	—	—	—
DTDA	105	—	—	—	—

[a] Two shifts are given in these cases as a result of split in the C=O stretch frequency in the complexes.

Talbe II. Electronic Spectral Data of Copper(II) Complexes.

Complex	Medium	Concentration $M \times 10^2$ (ε_M)	Peaks in Kk	Type
$CuCl_2$. TTDA	*a*		br. between ~13.3 and 11.4	IIa
	b	0.5(82), 0.25(82)	sh. ~13.2, ~11.2	IIa
		0.125 (76)	sh. ~12.8, ~11.4	IIa
		0.0625(65)	sh. ~12.8, ~11.2	IIa
$CuCl_2$. DTDA	*a*		br. ~13.2, v.br.sh. ~10.6	IIb
	b	0.5(92)	sh. ~12.9, br. ~11.6	IIa
	b	0.25(84), 0.1(80)	sh. ~12.9, br. ~11.6	IIa
	c	0.1(85), 0.05(85)	13.0, br.sh. ~ 10.9	IIb
$CuBr_2$. TTDA	*a*		20, v.br. between 14.3 and 10.8	III
$CuBr_2$. DTDA	*a*		20, br. between 13.9 and 11.8	III
	b	0.2	18.9(200*), 15.9(200, br. 11.5(102)	III
	c	0.2	18.9(300), 15.4(160), 13.3(160)	III
$Cu(NO_3)_2$. TTDA	*a*		13.9	IIc
	b	0.5(50), 0.25(50), 0.125(50)	12.8	IIc
$Cu(NO_3)_2$. DTDA	*a*		br. 13.2	IIc
	b	0.75(63), 0.25(60)	br. 13.1	IIc
	b	0.125(60)	13.2	IIc
	c	0.75(50)	13.3, sh. ~11.0	IIb
	c	0.25(50), 0.125(50)	13.7, sh. ~11.1	IIb
$Cu(ClO_4)_2$. 2TTDA	*a*		13.9	I
	b	1.0(42), 0.25(38), 0.125(38)	12.8	I
$Cu(ClO_4)_2$. 2DTDA	*a*		12.8	I
	b	1.0(55), 0.25(55), 0.125(64)	12.8	I
	c	1.0(90), 0.25(90), 0.125(90)	13.7	I
$CuCl_2$. TDPN	*a*		br. 12.5	IIc
	b	1.0(100)	11.4	IIc
$CuCl_2$. TDGA	*a*		v.b.r. between 11.1 and 6.3	IIa
	b	0.1(150)	sh. ~10.5, br. ~9.1	IIa
$CuCl_2$. 2IDPN	*a*		19.2, sh. 15.9	~I
	b	0.5(52)	11.4 br.	IIc
$Cu(BF_4)_2$. 2TTDA	*a*		13.3	I
	b	0.5(54)	12.3	I

[a] solid reflectance, [b] CH_3CN, [c] CH_2Cl_2. * For complexes having more than one peak, the molar extinction values are given in brackets behind the peaks in this column.

volving the S atom and the fact that these often are found in regions where a number of common vibrations occur, *e.g.* C–S stretching frequencies are found in the 600-700 cm^{-1} region.[17] A peak of medium intensity at approximately 1240 cm^{-1} was assigned to S–CH_2 wag in thio ethers containing the –CH_2SCH_2– or CH_3SCH_2– groupings.[18] Increases of about 20 cm^{-1} of a peak in this region, and relative decreases of the intensities upon complexation of the thio ether ligands, *viz.* TTDA, DTDA and TDPN, are interpreted as indicating bonded S atoms. This has been proved for TTDA by the structure determination of $CuCl_2$. TTDA (Figure 3). An increase of 40 cm^{-1} in the C≡N stretch frequency from 2260 to 2300 cm^{-1} upon complexation, is interpreted as bonding through both nitrogen atoms[19] of the two nitrile groups in $CuCl_2$. TDPN. In $CuCl_2$. 2IDPN the C≡N stretch frequency is the same as that of the free ligand (2260 cm^{-1}), which indicates that the cyanide groups are not bonded to the metal ion. However, the N–H stretch frequency is lowered by 110 cm^{-1} from 3315 cm^{-1} to 3205 cm^{-1}.[17] In $CuCl_2$. TDGA the C–O–C stretch

---

(18) I.F. Trotter and H.W. Thompson, *J. Chem. Soc.*, 481 (1946).

(19) K.W. Bagnall, D. Brown and P.J. Jones, *J. Chem. Soc.* (A) 1763. (1966).

frequency was unaltered upon complex formation, whereas the C=O stretch frequency was lowered by 30 cm^{-1}. Covalent nitrate peaks at 1470 and 1285 cm^{-1} [$Cu(NO_3)_2$. DTDA] as well as 1480 and 1300 cm^{-1} [$Cu(NO_3)_2$. TTDA] fall in the region usually interpreted as indicating monodentate nitrato groups.[20] Symmetrical peaks at 1075 cm^{-1} and 1030 cm^{-1} obtained in the infrared spectra of $Cu(ClO_4)_2$. 2TTDA and $Cu(BF_4)_2$. 2TTDA were assigned to ionic perchlorate[21] and tetrafluoroborate,[22] respectively.

Electronic Spectra and Structures. The electronic spectral data of the complexes are given in Table II. Molar extinction values for the solution spectra of complexes having a single peak are given in brackets behind their concentrations in the table. For those having multiple peaks ε_M values are given in brackets behind the peaks. (Fourth column, Table II). An investigation of the different experimental curves indicated that these curves can be divided into three different types, of which one type can be further divided into three closely related sub-types. A typical example of each of these types and subtypes of curves, *viz.* I, IIa, IIb, IIc, and III are represented in Figure 2. The reflectance spectra of two square pyramidal compounds previously published,[2] *viz.* those of [Cu(trien)-SCN]CNS (curve A) and $Cu(NH_3)_5(BF_4)_5$ (curve B) are also reproduced in Figure 2, for comparison purposes.

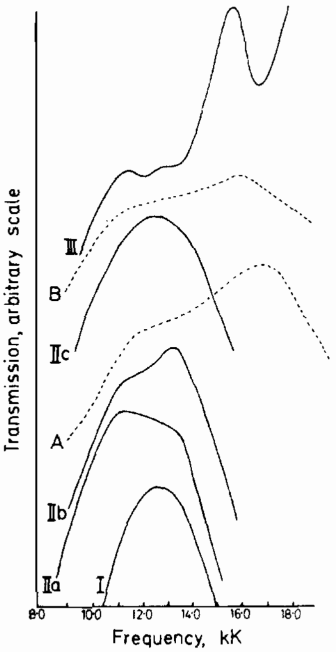

Figure 2. Electronic spectra obtained for typical copper(II) complexes.

Curve I - $Cu(ClO_4)_2$. 2TTDA (0.01*M* solution in CH_3CN)
Curve IIa - $CuCl_2$. TTDA (0.005*M* solution in CH_3CN)
Curve IIb - $Cu(NO_3)_2$. DTDA (0.0075*M* solution in CH_2Cl_2)
Curve IIc - $CuCl_2$. TDPN (0.01*M* solution in CH_3CN)
Curve III - $CuBr_2$. DTDA (0.002*M* solution in CH_2Cl_2)
Curve A - [Cu(trien)SCN]CNS (solid reflectance)
Curve B - $[Cu(NH_3)_5](BF_4)_2$ (solid reflectance)

Structural similarities between the solid states and their methylene dichloride solutions (DTDA complexes only) are indicated by the very close resemblance between their electronic spectra in these different circumstances. Methyl cyanide solutions of concentrations higher than 0.002 *M*, generally show only small differences when compared to their corresponding solid reflectance spectra, but become increasingly different from the latter upon dilution, mainly with respect to a lowering of ε_M values, except for $Cu(ClO_4)_2$. 2DTDA where a slight increase in ε_M value is obtained upon dilution (Table II). Similar changes in methyl cyanide solution spectra are also observed for $CuCl_2$. DTDA, $CuBr_2$. DTDA and, to a smaller extent, for $CuCl_2$. TDPN whereas Beer's Law is followed for dilutions in methylene dichloride.

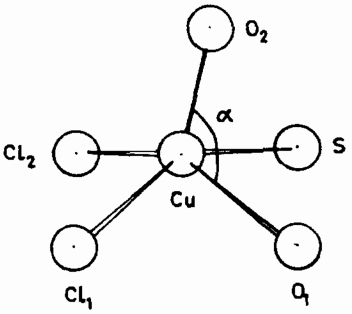

Figure 3. A sketch of molecular structure of $CuCl_2$. TTDA.

A single crystal X-ray analysis of $CuCl_2$. TTDA[16] indicated a slightly distorted square pyramidal structure with the two chloride ions, one amide oxygen atom and the thioethereal sulphur atom almost exactly coplanar and the copper atom 0.21 Å above the plane. The angle α (Figure 3) is 85.7°. For the purpose of considering its ligand field spectrum, this complex can be regarded as having essentially C_{4v} symmetry.

Ciampolini recently pointed out[2] that the electronic spectra of CuN_5 chromophores with essentially C_{4v} symmetry, appear to be quite different from those with essentially D_{3h} symmetry. The electronic spectrum of $CuCl_2$. TTDA (i) (Figure 2, Type IIa) *i.e.* an essentially square pyramidal $CuCl_2O_2S$ chromophore, is similar to that of [Cu(trien)SCN]CNS (ii) (Figure 2, curve A), *i.e.* an essentially square pyramidal CuN_4S chromophore, and fairly similar to square pyramidal $Cu(NH_3)_5(BF_4)_2$ (Figure 2, curve B). The only important differences between the spectra of (i) and (ii) are that (ii) is shifted to higher energies and is also broader than (i). Both of these fact can be ascribed to the higher ligand field of the 5N grouping as compared to the 2ClS2O grouping.

The electronic spectrum of $CuCl_2$. DTDA, as well as all other Type IIb spectra, is also very similar to that published for $Cu(NH_3)_5(BF_4)_2$ (Figure 2, curve B). In the light of these similarities, all the compounds with Type II (a, b and c) spectra are, therefore, taken to have essentially C_{4v} symmetry. The molar extinction values of these compounds which are all bigger than 45, are in agreement with such acentric molecules.[23]

---

(20) N.F. Curtis and Y.M. Curtis, *Inorg. Chem.*, *4*, 884 (1965).
(21) B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.*, 3091 (1961).
(22) D.H. Brown, R.H. Nuttall, J. McAvry, and D.W.A. Sharp, *J. Chem. Soc.*, (*A*), 892 (1966).

It appears that the $Cu(NO_3)_2$. TTDA complex is slightly different in structure from that of the $CuCl_2$ and $CuBr_2$ complexes of TTDA if the small differences in electronic spectra are borne in mind as well as the absence of the splitting in the C=O stretch frequencies (Table I). The $Cu(NO_3)_2$. DTDA and $CuCl_2$. DTDA complexes both have Type IIb spectra in CH_2Cl_2 solution and are even more similar although the differences in C=O stretch frequencies still exist (Table I). The electronic spectra of $CuBr_2$. TTDA and $CuBr_2$.DTDA (Type III) differ from Type II spectra only in that a charge transfer band is near to the ligand field bands of the bromo complex, and by the increase in the molar extinction due to intensity stealing. The electronic and i.r. spectral data, in which similar splittings in the carbonyl stretch frequencies (Table I) have been obtained, indicate that these two bromo complexes have structures very similar to those of their chloro analogues. Generally speaking, Type I spectra have narrower and more symmetrical bands at relatively higher energies and lower molar extinction values than the other types. This is typical of tetragonally distorted octahedral copper(II) compounds (D_{4h} symmetry).[23] The unexpected high ε_M value for $Cu(ClO_4)_2$. 2DTDA may be ascribed to a distortion which removes the centre of symmetry, due possibly to the bulky size of the ligand.

$CuCl_2$. 2IDPN can have a six-coordinate structure if chlorine bridging takes place, since no evidence could be found from i.r. data that the cyanide nitrogen atoms of the ligand act as donor atoms. The methyl cyanide solution spectrum is quite different from that of the solid reflectance and similar to the other penta-coordinate species. (See Table II for peaks).

Magnetic Properties. The magnetic moments of the most typical and stable compounds and the temperatures at which these were determined, are given in Table I. The moments of complexes believed to have penta-coordinate structures, vary between 1.77 and 1.88 B.M. whereas those believed to have distorted octahedral structures, vary between 1.69 and 1.72 B.M. All of these proved to be field indenpendent at room temperature and are within the range normally observed for copper(II) complexes having orbitally non-degenerate ground states ($^2B_1$ in both C_{4v} and D_{4h} symmetries).[20]

$CuCl_2$. TTDA follows the Curie-Weiss law between 295°K and 98°K with a θ-value of $-37°$.

Comparison of the Ligands. The thiodiacetamide ligands (TTDA and DTDA) form the most stable complexes of those studied. There is almost no difference in stabilities between the complexes of these except that $CuBr_2$. DTDA is indefinitely stable whereas $CuBr_2$. TTDA slowly decomposes upon standing. When the thio ether S atom is replaced by an oxygen atom, donation through the oxygen atom (see discussion of i.r. data) does not occur towards $CuCl_2$. TDGA complex with an electronic spectrum typical of tetrahedral copper(II) (Table II)[24] is obtained. Amongst the other ligands (Figure 1) DCE is so weak that its $CuCl_2$ complex could not be isolated from methyl cyanide solution. TDPN forms the penta-coordinate $CuCl_2$. TDPN complex which can readily be isolated whereas IDPN forms stable crystals of $CuCl_2$. 2IDPN in which only the NH group acts as a Lewis base. This again stresses the increasing basicity in the order ethereal oxygen < thio ethereal S < imino nitrogen atom.

Acknowledgment. The authors wish to thank the South African Council for Scientific Research, the South African Atomic Energy Board, and the University of Port Elizabeth for financial assistance received.

---

(23) A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier Publishing Co., London (1968), p. 356.

(24) B.N. Figgis and J. Lewis, Progress in Inorganic Chemistry, Interscience, New York, 1964, Vol. 6, p. 217.