Table XI. Comparison of Magnetic Properties for Some Binuclear Nickel(II) Triketonates

compd	temp range, K	Θ_p, K	g_{av}[a]	g[b]	J, cm^{-1}	ref
$[Ni_2(DBA)_2(py)_4]\cdot 4py$	77–298			2.0	−13	17
$[Ni_2(BAA)_2(OH_2)_4]\cdot H_2O$	77–400	−30	2.42	2.40	−10	17
$[Ni_2(DBA)_2(OH_2)_4]$	297–421	−30	2.46	2.46	−8	17
$[Ni_2(TFDAA)_2(py)_4]$	166–300	−80	2.37	2.39	−26	this work

[a] Calculated from $C = N\beta^2g^2[S(S+1)]/3k$ for the paramagnetic region. $S = 1$. [b] This is the g value used to determine J.

the basis of structural factors. The only structural factor that is a variable in the copper compounds is the deviation of the coppers from the ligand plane, and the deviation is greatest for $Cu_2(DAA)_2(py)_2$. In addition, $Cu_2(DTFACP)_2(H_2O)_2$ and $Cu_2(HXFDAA)_2(CH_3OH)_2$ both contain CF_3 substituent groups and have very similar structural parameters except for a marked difference in coplanarity (0.10 vs. 0.20 Å deviation from planarity). Yet, the strength of the magnetic exchange is appreciably different; the more planar arrangement exhibits the strongest exchange. This trend is reasonable since one would expect a more favorable orbital overlap in the planar case. Thus, one expects that the anomalous behavior of $Cu_2(DAA)_2(py)_2$ is due to the coppers being 0.28 Å out of the ligand plane and that this factor is considerably more important than the electronic effects of the CH_3 groups.

Pertinent magnetic data for four binuclear nickel(II) triketonates have been collected in Table XI. Based on the structural data available (Table IX) it is reasonable to presume that the in-plane environments of the Ni(II) ions are virtually identical in the four compounds. There are some problems with the direct comparison of the properties of $Ni_2(DBA)_2(py)_4$ and the other three compounds since the value of g required in the calculation of J is unusually low. In addition, there is a peculiar temperature dependence for $Ni_2(DBA)_2(H_2O)_4$ that is difficult to explain,[17] since it is not possible to fit the experimental results in the 4.2–421 K range with single values of g and/or J. The values shown in Table XI for $Ni_2(DBA)_2(H_2O)_4$ are for the generally more reliable high-temperature region. These problems and the lack of sufficient data make strong conclusions impossible. However, qualitatively it appears at this point that in binuclear Ni(II) complexes the trifluoromethyl-substituted compounds exhibit exchange at least as strong as the others.

No detailed analysis of the complex d^7–d^7 exchange in the binuclear cobalt(II) triketonates has been reported. Still a direct comparison between the $Co_2(DBA)_2(py)_4$[18] magnetic moments and those of $Co_2(TFDAA)_2(py)_4$ should be instructive since the structures are likely to be extremely similar. For $Co_2(DBA)_2(py)_4$, the μ_{eff} is 4.07 μ_B at 300 K and 3.36 μ_B at 77 K. For $Co_2(TFDAA)_2(py)_4$, the μ_{eff} is 4.62 μ_B at 300 K and 3.74 μ_B at 77 K. The larger magnetic moments for the CF_3-, CH_3-substituted complex may be the result of the electronic effect of these groups compared to the effect of the phenyl groups in $Co_2(DBA)_2(py)_4$. Due to the paucity of data it is not possible to comment further at this time.

Acknowledgment is made to the National Science Foundation, Grant CHE-77-02664, for support of this research. J.W.G. gratefully acknowledges support from the Lubrizol Corp. in the form of a research fellowship.

Registry No. $Cu_2(HXFDAA)_2(CH_3OH)_2$, 74096-91-6; $Ni_2(TFDAA)_2(py)_4$, 74113-00-1; $Cu_2(HXFDAA)_2(H_2O)_2$, 74113-01-2; $Cu_2(TFDAA)_2(CH_3OH)_2$, 74096-92-7; $Ni_2(HXFDAA)_2(H_2O)_4$, 62560-16-1; $Co_2(TFDAA)_2(py)_4$, 74096-93-8.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratorium für Anorganische Chemie, ETH, CH-8092 Zürich, Switzerland,
the Department of Chemistry and Biochemistry, James Cook University of North Queensland, Queensland 4811, Australia,
and the Department of Chemistry, Polytechnic of North London, London N7 8DB, United Kingdom

Metal-Ion Recognition by Macrocyclic Ligands. Synthetic, Thermodynamic, Kinetic, and Structural Aspects of the Interaction of Copper(II) with 14- to 17-Membered Cyclic Ligands Containing an O_2N_2-Donor Set

KENNETH R. ADAM,[1a] GIORGIO ANDEREGG,[1b] LEONARD F. LINDOY,*[1a] HYACINTH C. LIP,[1a] MARY McPARTLIN,[1c] JOHN H. REA,[1a] ROLAND J. SMITH,[1a] and PETER A. TASKER*[1c]

Received December 26, 1979

As part of a general study of the use of mixed-donor macrocycles as metal-ion-specific reagents, the interaction of copper(II) with a series of 14- to 17-membered macrocycles containing an O_2N_2-donor set has been investigated. The investigation parallels previous studies involving nickel complexes of this series of ligands. Copper complexes having both 1:1 and 1:2 metal to ligand ratios form under appropriate conditions. The kinetics of dissociation of the 1:1 complexes in HCl (I = 0.1) in 95% methanol have been studied, and the respective thermodynamic stabilities have been determined potentiometrically by the pH titration method. In contrast to the nickel complexes which show a peak in both the kinetic and thermodynamic stabilities at the 16-membered ring complex, the copper complexes show no definite ring-size discrimination effects; this different behavior is discussed in terms of the respective structures of these two sets of complexes. Solution studies indicate that all the macrocycles form five-coordinate complexes of type $[Cu(macrocycle)Cl]^+$, and the solid-state structure of the perchlorate salt of one such complex (containing the 15-membered macrocycle) has been determined by X-ray diffraction. The coordination sphere of the copper consists of the four donor atoms of the macrocycle together with a chloride ion. The copper ion sits above the hole of the macrocycle which is coordinated in a bent conformation.

Introduction

Typically, macrocyclic ligands containing nitrogen donors (including several natural macrocycles) show strong tendencies to complex transition-metal ions.[2] In contrast, those incorporating only oxygen donor atoms (the crown polyethers) prefer non transition metal ions such as the alkali or alkaline earth ions.[3,4]

---

[1] (a) James Cook University of North Queensland. (b) ETH, Zürich. (c) Polytechnic of North London.

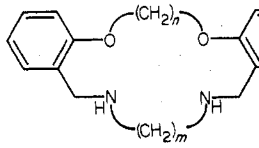
[2] Lindoy, L. F. *Chem. Soc. Rev.* **1975**, *4*, 421.

[3] Lehn, J. M. *Struct. Bonding (Berlin)* **1973**, *16*, 1. Anderegg, G. *Helv. Chim. Acta* **1975**, *58*, 1218.

[4] Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351.

0020-1669/80/1319-2956$01.00/0 © 1980 American Chemical Society

Apart from this ability to discriminate between metal ions from different areas of the periodic table on the basis of donor atom type, variation of the macrocycle ring size can also lead to enhanced specificity for particular metal ions.[3-5] For example, it has been clearly demonstrated that ring-size variation within the O_2N_2-donor macrocycles **1**–**4**[6,7] markedly influences the kinetic[8] and thermodynamic[9] behavior of the respective nickel complexes. Along the 14- to 17-membered ligand series, the 16-membered macrocycle yields the most kinetically inert complex as well as the most thermodynamically stable complex; from comparison of X-ray structures[9,10] of the nickel(II) complexes of the 15- and 16-membered macrocycles, it appears[8] that the 16-membered macrocycle provides the ring of least strain for nickel(II). Nevertheless, the presence of two ether oxygen donors in the ligands is reflected by lower kinetic and thermodynamic stabilities for their nickel complexes than those which occur for related nickel complexes of N_4-donor macrocycles.[4,5] Indeed, in contrast to the O_2N_2-donor ligand complexes, the N_4-donor nickel complexes are often so stable that it has proved difficult to obtain reliable kinetic and thermodynamic data in certain cases.[11]



ligand	*n*	*m*	abbreviation
1	2	2	O-en-N-enH_4
2	2	3	O-en-N-tnH_4
3	3	3	O-tn-N-tnH_4
4	4	3	O-bn-N-tnH_4

As a continuation[6,8-10,12] of the general study of the potential of ligands incorporating oxygen and nitrogen donor atoms for metal-ion recognition (kinetic or thermodynamic), we now report an investigation of the interaction of copper(II) with macrocycles **1**–**4**.

Experimental Section

Synthesis and Characterization of the Complexes. Conductance measurements were determined by using a Philips conductivity bridge, Type PR 9500. All measurements were recorded at 25 °C on solutions approximately 10^{-3} M. Infrared spectra were recorded by using Nujol mulls with a Perkin-Elmer 197 spectrophotometer. All spectra were calibrated by using a polystyrene standard. Solution spectra (in dimethyl sulfoxide) were obtained by using a Beckman ACTA-IV spectrophotometer. Solid-state spectra were determined by using Nujol mulls of the compound spread on filter paper with use of the above spectrophotometer. The dimethyl sulfoxide used for the conductances and spectrophotometric studies was AR grade which was redistilled and stored over 4-Å molecular sieves. Dimethyl sulfoxide was chosen because other common solvents led, in some cases, to precipitation before completion of the respective titrations. Magnetic moments were determined by using a Faraday balance calibrated against $Hg[Co(NCS)_4]$. Microanalyses for C, H, and N were determined by Mr. J. Kent, Department of Chemistry, University of Queensland. Copper analyses were determined by using a Varian AA6 atomic absorption spectrophotometer. Analytical results are listed in the supplementary data. All compounds were dried over P_2O_5 in a vacuum.

(3,4:9,10-Dibenzo-1,12-diaza-5,8-dioxacyclotetradecane)copper(II) Perchlorate [Cu(O-en-N-enH_4)$(ClO_4)_2$]. O-en-N-enH_4 (0.30 g) in hot methanol (30 mL) was added to a stirred boiling solution of copper(II) perchlorate hexahydrate (1.10 g) in butanol (40 mL). The product separated as an olive green solid which was filtered off and washed with cold ethanol; yield 60%. The product was recrystallized from a methanol/butanol mixture and then washed with ether.

(3,4:9,10-Dibenzo-1,12-diaza-5,8-dioxacyclotetradecane)copper(II) Chloride Hemihydrate [Cu(O-en-N-enH_4)Cl_2·$^1/_2H_2O$]. In a manner similar to the above using copper(II) chloride dihydrate (0.17 g), a blue-green solid was isolated; yield 50%. It was recrystallized from a methanol/ethanol mixture.

(3,4:9,10-Dibenzo-1,12-diaza-5,8-dioxacyclopentadecane)copper(II) Perchlorate [Cu(O-en-N-tnH_4)$(ClO_4)_2$]. O-en-N-tnH_4 (0.31 g) in hot methanol (30 mL) was added to a stirred boiling solution of copper(II) perchlorate hexahydrate (1.10 g) in methanol (30 mL). The green solution was filtered while hot and then allowed to cool. The green crystals were washed with methanol and then ether; yield 55%.

Chloro(3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane)copper(II) Perchlorate [[Cu(O-en-N-tnH_4)Cl]ClO_4]. In a manner similar to the above, a mixture of copper(II) perchlorate hexahydrate (0.37 g) and lithium chloride (0.09 g) in methanol (30 mL) yielded green crystals, yield 65%.

(3,4:9,10-Dibenzo-1,12-diaza-5,8-dioxacyclopentadecane)copper(II) Chloride [Cu(O-en-N-tnH_4)Cl_2]. O-en-N-tnH_4 (0.31 g) in warm methanol (10 mL) was added to a stirred warm solution of copper(II) chloride dihydrate (0.17 g) in methanol (30 mL). After 2 h the purple product was filtered off and washed with methanol and then ether; yield 60%.

(3,4:10,11-Dibenzo-1,13-diaza-5,9-dioxacyclohexadecane)copper(II) Perchlorate [Cu(O-tn-N-tnH_4)$(ClO_4)_2$]. O-tn-N-tnH_4 (0.32 g) in hot methanol (30 mL) was added to a stirred boiling solution of copper(II) perchlorate hexahydrate (1.10 g) in methanol (40 mL). Butanol was slowly added to the boiling mixture until a green solid began to separate. After the solution was cooled, the product was filtered off and washed with ether; yield 35%.

(3,4:10,11-Dibenzo-1,13-diaza-5,9-dioxacyclohexadecane)copper(II) Chloride Hemihydrate [Cu(O-tn-N-tnH_4)Cl_2·$^1/_2H_2O$]. O-tn-N-tnH_4 (0.32 g) in hot absolute ethanol (40 mL) was added slowly to a stirred boiling solution of copper(II) chloride (0.14 g) in absolute ethanol (40 mL). The volume was reduced to 50 mL. After 3 h of standing, a mixture of green and purple products separated. After several washings with ethanol, only the blue-green crystals remained. The product was collected and washed with ether; yield 25%.

(3,4:11,12-Dibenzo-1,14-diaza-5,10-dioxacycloheptadecane)copper(II) Chloride [Cu(O-bn-N-tnH_4)Cl_2]. O-bn-N-tnH_4 (0.17 g) in hot ethanol (70 mL) was added to a stirred boiling solution of copper(II) chloride (0.07 g) in butanol (20 mL). The greenish blue solid which separated on standing was collected and washed with ethanol and then ether; yield 40%.

(3,4:11,12-Dibenzo-1,14-diaza-5,10-dioxacycloheptadecane)copper(II) Bromide [Cu(O-bn-N-tnH_4)Br_2]. O-bn-N-tnH_4 (0.17 g) in hot methanol (40 mL) was added to a stirred boiling solution of copper(II) bromide (0.11 g) in methanol (60 mL). When the mixture was allowed to stand, green microcrystals separated. They were filtered off and washed with methanol and then ether; yield 55%.

X-ray Crystallography. Crystal data: $C_{19}H_{24}Cl_2CuN_2O_6$, mol wt 447.312, monoclinic, space group[13] $P2_1/n$, $a = 11.757$ (2) Å, $b = 18.325$ (3) Å, $c = 10.396$ (2) Å, $\beta = 108.16$ (2)°, $V = 2128.3$ Å^3, $T = 22$ °C, $Z = 4$, $d(\text{calcd}) = 1.396$ g cm^{-3}.

Data were collected with a crystal of dimensions ca. 0.25 × 0.18 × 0.22 mm by using a Philips PW1100 four-circle diffractometer with Mo Kα radiation ($\lambda = 0.71069$ Å) from a graphite monochromator. A θ–2θ scan mode was used, and 6703 reflections in one quadrant ($\pm h,k,l$) within the θ range of 3–30° were examined. Weak reflections which gave $I_t - 2(I_t)^{1/2} < I_b$ on the first scan were not recorded (I_t = count rate at the top of the reflection peak and I_b = the mean count rate of two preliminary 5-s background measurements on either side

---

(5) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392.

(6) Armstrong, L. G.; Grimsley, P. G.; Lindoy, L. F.; Lip, H. C.; Norris, V. A.; Smith, R. J. *Inorg. Chem.* **1978**, *17*, 2350.

(7) Grimsley, P. G.; Lindoy, L. F.; Lip, H. C.; Smith, R. J.; Baker, J. T. *Aust. J. Chem.* **1977**, *30*, 2095.

(8) Ekstrom, A.; Lindoy, L. F.; Smith, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 4014. Ekstrom, A.; Lindoy, L. F.; Smith, R. J. *Inorg. Chem.* **1980**, *19*, 724.

(9) Adam, K. R.; Lindoy, L. F.; Smith, R. J.; Anderegg, G.; Henrick, K.; McPartlin, M.; Tasker, P. A. *J. Chem . Soc., Chem. Commun.* **1979**, 812.

(10) Ekstrom, A.; Lindoy, L. F.; Lip, H. C.; Smith, R. J.; Goodwin, H. J.; McPartlin, M.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1027.

(11) See for example: Hertli, L.; Kaden, T. *Helv. Chim. Acta* **1974**, 57, 1328. Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Inorg. Chem.* **1978**, *17*, 1042.

(12) Armstrong, L. G.; Lindoy, L. F. *Inorg. Chem.* **1975**, *14*, 1322. Lindoy, L. F.; Lip, H. C.; Power, L. F.; Rea, J. H. *Inorg. Chem.* **1976**, *15*, 1724. Armstrong, L. G.; Lindoy, L. F.; McPartlin, M.; Mockler, G. M.; Tasker, P. A. *Inorg. Chem.* **1977**, *16*, 1665.

(13) Equivalent positions: x, y, z; $-x, -y, -z$; $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; and $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$. The standard $P2_1/c$ cell has $a = 10.396$ Å, $b = 18.325$ Å, $c = 13.044$ Å, and β 121.08°. Unit cell parameters were obtained from a least-squares fit of the setting angles of 25 reflections with 2θ values ca. 20°.

of the peak). Of the remaining 2935 reflections those for which the total intensity recorded in the first scan (I_i) was <500 counts were scanned a second time. A constant scan speed of 0.05° s^{-1} and a scan width of 1.0° were used, with a background measuring time proportional to I_b/I_i. Three standard reflections were measured every 6 h during data collection and showed no significant variation in intensity.

The standard deviation of the intensity (I) was taken as $[\sigma_c(I)^2 + (0.04I)^2]^{1/2}$, where $\sigma_c(I)$ is the standard deviation from counting statistics and the term in I^2 was introduced to allow for other sources of error. I and $\sigma(I)$ were corrected for Lorentz and polarization factors with use of a program written for the PW1100 diffractometer, and equivalent reflections were averaged, giving a total of 2514 data with $I/\sigma(I) \geq 3.0$. Absorption corrections were not applied.

The copper and the two chlorine atoms were located from a Patterson synthesis. Least-squares refinement of these positional and isotropic thermal parameters together with the overall scale factor gave $R = 0.37$. The positions of all atoms except hydrogen and those of the perchlorate oxygen atoms were readily obtained from a difference Fourier synthesis calculated at this stage. Refinement of the atom coordinates and isotropic parameters gave $R = 0.25$. A difference Fourier synthesis revealed three areas of electron density spanning a range of possible positions for the remaining perchlorate oxygen atoms and indicating restricted rotation of the perchlorate anion about one Cl–O bond. No program was available which would accurately take account of this behavior. Close examination of the electron density distribution revealed the three local maxima corresponding to a preferred orientation of the anion, so the remaining oxygen atoms were assigned these positions. Three cycles of refinement of the atomic coordinates and isotropic thermal parameters of the perchlorate atoms reduced R to 0.105. Anisotropic thermal parameters were assigned to the metal atom, the atom directly bonded to it, and the atoms of the perchlorate anion. Eight cycles of refinement with the cation and anion in different blocks gave $R = 0.084$. A difference Fourier calculated at this stage showed diffuse maxima corresponding to reasonable positions for hydrogen atoms. In the final cycles of refinement the hydrogen atoms were included in calculated positions "riding" on the atoms to which they are bonded at a fixed distance of 1.08 Å. A common isotropic thermal parameter was assigned to the phenylene hydrogen atoms and another to the remaining hydrogen atoms; these two parameters were included as free variables in the refinement. This resulted in $R = 0.0748$ and $R_w = 0.0784$ $[R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|]$, where w was the weight assigned to each reflection as $w = 1/\sigma^2(F_o)$; the maximum shift was 0.109σ, and the average shift was 0.018σ. The final difference Fourier map showed diffuse regions of electron density of ca. 0.5 e Å^{-3} in the region of the perchlorate oxygen atoms.

Major computations were performed by using the SHELX program.[14] The neutral-atom scattering factors used were taken from ref 15 and were corrected for both the real and imaginary anomalous scattering contributions.[16] Atomic positional and thermal parameters are given in Tables I and II.

log *K* Determinations. The apparatus and conditions [95% methanol; $I = 0.1$, $(CH_3)_4NCl$][17] for determination of the stability constants were identical with those used previously for analogous studies involving nickel complexation.[18] The apparatus was calibrated daily to yield E_0 and pK_w values for the system by titration of a solution containing HCl (4.00 × 10^{-3} M) and tetramethylammonium chloride (0.1 M; Fluka, puriss) in 95% methanol with standardized tetramethylammonium hydroxide (0.1 M) in 95% methanol. The tetramethylammonium hydroxide was prepared by the literature procedure.[19]

Table I. Refined Atomic Positional and Isotropic Thermal Parameters

atom	x^a	y	z	U,^{b} Å^2
Cu	−1408 (1)	365 (1)	1643 (1)	
Cl(1)	511 (2)	−230 (1)	2159 (2)	
O(1a)	−638 (4)	1282 (3)	2677 (5)	
O(1b)	−1692 (5)	167 (3)	3556 (5)	
N(1a)	−1820 (5)	885 (3)	−133 (6)	
N(1b)	−2264 (6)	−526 (3)	851 (6)	
C(1a)	−299 (7)	1139 (4)	4140 (8)	42 (2)
C(2a)	243 (7)	1584 (4)	2189 (8)	40 (2)
C(3a)	1417 (7)	1673 (4)	2970 (9)	49 (2)
C(4a)	2250 (9)	1937 (5)	2359 (9)	65 (3)
C(5a)	1864 (8)	2113 (5)	1024 (9)	58 (2)
C(6a)	690 (7)	2026 (5)	256 (9)	53 (2)
C(7a)	−175 (7)	1759 (4)	818 (8)	41 (2)
C(8a)	−1447 (7)	1668 (4)	19 (9)	49 (2)
C(9a)	−3070 (7)	804 (5)	−1051 (9)	54 (2)
C(1b)	−1374 (7)	826 (4)	4392 (8)	44 (2)
C(2b)	−2607 (6)	−277 (4)	3715 (8)	41 (2)
C(3b)	−3160 (7)	−152 (4)	4689 (8)	49 (2)
C(4b)	−4007 (7)	−638 (5)	4836 (9)	54 (2)
C(5b)	−4304 (8)	−1248 (5)	4009 (9)	58 (2)
C(6b)	−3742 (7)	−1374 (5)	3048 (9)	57 (2)
C(7b)	−2877 (7)	−890 (4)	2877 (8)	44 (2)
C(8b)	−2200 (7)	−1090 (5)	1926 (8)	50 (2)
C(9b)	−3492 (7)	−416 (5)	−80 (8)	52 (2)
C(9c)	−3456 (8)	16 (5)	−1304 (9)	57 (2)
Cl(2)	5872 (3)	1846 (2)	1868 (3)	
O(21)	6286 (7)	1122 (4)	1693 (8)	
O(22)	5227 (14)	2104 (6)	673 (16)	
O(23)	6848 (8)	2254 (5)	2541 (14)	
O(24)	5091 (9)	1785 (9)	2579 (14)	

[a] Fractional coordinates × 10^4. The standard deviation of the least significant digit is included in parentheses in this and subsequent tables. [b] Isotropic thermal parameters × 10^3. Anisotropic thermal parameters are given in Table II.

log K values were obtained from titration of a solution of the complex ((0.15–0.25) × 10^{-3}M) in calibration solution with tetramethylammonium hydroxide (0.1 M). Titration steps of between 0.02 and 0.2 mL were chosen such that the millivolt changes between successive points did not exceed 10.0 mV. With use of the titration data within the approximate pH range 4.5–6.5, together with the protonation constants for the respective ligands determined previously,[9,18] stability constants for the complexes were calculated by using the program "KONST".[20] Each value quoted is the mean of four separate determinations involving at least two different complex concentrations.

Kinetics of Ligand Dissociation. The copper complex in 95% methanol was mixed, by using the computer-interfaced stopped-flow system described elsewhere,[21] with an equal volume of 95% methanol containing hydrochloric acid (0.2 M) [or containing hydrochloric acid (0.1 M) and $N(CH_3)_4Cl$ (0.1 M)]. The following wavelengths were used for the dissociation studies (ligand, λ (nm)): **1**, 670; **2**, 680; **3**, 650; **4**, 700. For two complexes the dissociations were too fast to be followed by the stopped-flow technique. The first-order rate constants for the dissociations in excess acid were derived from fits to

$$\ln (A_t - A_\infty) = -k_{obsd}t + \text{constant} \qquad (1)$$

where A_t and A_∞ are the absorbances of the solution at time t and at infinity, respectively. The rate constants quoted are the average of between six and nine determinations.

Results and Discussion

Synthesis and Characterization of the Solid Complexes. The O_2N_2-donor macrocycles **1–4** were prepared and characterized as described previously.[7] Copper(II) complexes of these 14- to 17-membered macrocycles were synthesized by the addition of the respective ligands to the corresponding copper salts in methanol, ethanol, or butanol. The complexes isolated are listed in Table III. In contrast to other copper salts, copper chloride initially gave a mixture of complexes with these ligands; the mixture consisted of two complexes, a green-blue product and a dark blue or purple product. However, subsequent purification led to the isolation of only one complex in each case; with O-en-N-tnH_4, a purple complex was isolated

---

(14) Sheldrick, G. M. "SHELX-76 Program System"; University Chemical Laboratory: Cambridge, U.K.; 1976.

(15) Doyle, P. A.; Turner P. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 390.

(16) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(17) Because of low solubilities and hydrolysis reactions in water, attempts to undertake comparative log *K* studies in aqueous media were unsuccessful.

(18) Anderegg, G.; Ekstrom, A.; Lindoy, L. F.; Smith, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 2670.

(19) Walker, J.; Johnson, J. *J. Chem. Soc.* **1905**, *87*, 955.

(20) Anderegg, G. *Helv. Chim. Acta* **1961**, *44*, 1673.

(21) Ekstrom, A. *Inorg. Chem.* **1973**, *12*, 2455.

Table II. Anisotropic Thermal Parameters ($Å^2 \times 10^3$)

	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu[b]	610 (7)	414 (5)	245 (4)	−62 (5)	74 (4)	8 (4)
Cl(9)	53 (1)	63 (1)	36 (1)	10 (1)	17 (1)	−4 (1)
O(1a)	50 (3)	44 (3)	26 (3)	−6 (2)	12 (2)	0 (2)
O(1b)	65 (4)	37 (3)	29 (3)	−11 (3)	24 (3)	−9 (2)
N(1a)	51 (4)	47 (4)	23 (3)	5 (3)	12 (3)	0 (3)
N(1b)	61 (4)	48 (4)	33 (3)	−7 (3)	18 (3)	−7 (3)
Cl(2)	80 (2)	79 (2)	80 (2)	−14 (2)	33 (2)	−33 (2)
O(21)	130 (7)	75 (5)	80 (5)	−1 (5)	41 (5)	−22 (4)
O(22)	316 (18)	114 (9)	205 (15)	74 (11)	22 (14)	77 (10)
O(23)	102 (7)	90 (6)	297 (15)	32 (6)	51 (9)	−84 (9)
O(24)	116 (8)	391 (22)	231 (14)	99 (11)	118 (10)	−192 (15)

[a] Expressed in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] The values for Cu are given $\times 10^4$.

Table III. Physical Data for the Complexes

compd	color	selected IR abs, cm^{-1}			μ, μ_B	Λ,[a] S cm^2 mol^{-1}	vis spectra[b] (solid state) nm
		H_2O	amine	ClO_4^-			
$Cu(O\text{-}en\text{-}N\text{-}enH_4)(ClO_4)_2$	olive green		3240	1110, 1060	1.82[c]	61	700
$Cu(O\text{-}en\text{-}N\text{-}enH_4)Cl_2 \cdot {}^1/_2H_2O$	blue-green	3450	3300, 3160		1.80	25	735
$Cu(O\text{-}en\text{-}N\text{-}tnH_4)(ClO_4)_2$	green		3210	1120, 1045	1.92	64[d]	650
$[Cu(O\text{-}en\text{-}N\text{-}tnH_4)Cl]ClO_4$	green		3235, 3085	1080	1.88	31[e]	725
$Cu(O\text{-}en\text{-}N\text{-}tnH_4)Cl_2$	purple		3255		1.82	24	535
$Cu(O\text{-}tn\text{-}N\text{-}tnH_4)(ClO_4)_2$	green		3210	1120, 1050	1.88	61	655
$Cu(O\text{-}tn\text{-}N\text{-}tnH_4)Cl_2 \cdot {}^1/_2H_2O$	green-blue	3400	3270, 3180		1.83	23	645
$Cu(O\text{-}bn\text{-}N\text{-}tnH_4)Cl_2$	green-blue		3270, 3180		1.89	23	645
$Cu(O\text{-}bn\text{-}N\text{-}tnH_4)Br_2$	green		3250, 3160		2.05	36	655

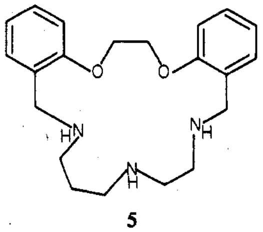
[a] Ca. 10^{-3} M in dimethyl sulfoxide at 26 °C; expected[30] range for a 1:1 electrolyte: 23–42 S cm^2 mol^{-1}. [b] Maximum of a broad envelope of bands. [c] At 24 °C. [d] In acetonitrile a value of 298 S cm^2 mol^{-1} (expected[30] 220–300 S cm^2 mol^{-1} for a 2:1 electrolyte) and in dimethylformamide a value of 145 S cm^2 mol^{-1} (expected[30] 130–170 S cm^2 mol^{-1} for a 2:1 electrolyte) were obtained. [e] In acetonitrile a value of 151 S cm^2 mol^{-1} (expected[30] 120–160 S cm^2 mol^{-1} for a 1:1 electrolyte) and in dimethylformamide a value of 83 S cm^2 mol^{-1} (expected[30] 65–90 S cm^2 mol^{-1} for a 1:1 electrolyte) were obtained.

whereas, with each of the other three ligands, the green-blue complex was obtained. The structures of these products are discussed later.

The three diperchlorate complexes each show a split perchlorate band at ~1100 cm^{-1} (Table III). This may reflect different environments in these complexes arising from crystal packing or hydrogen bonding effects; however, the splitting could reflect a lowering of the symmetry of the perchlorate group owing to coordination to the copper ion. In contrast, the infrared spectrum of $[Cu(O\text{-}en\text{-}N\text{-}tnH_4)Cl]ClO_4$[22] contains only a single absorption which is typical of noncoordinated perchlorate anions and which is in accord with the X-ray diffraction structure of this complex (see later). All complexes have room-temperature magnetic moments in the range expected for copper(II) with $S = {}^1/_2$ (Table III).

The solid-state visible spectra all show a broad envelope of bands in the region 500–1000 nm (λ_{max} values are listed in Table III). For copper(II) complexes having regular tetragonal (D_{4h}), trigonal-bipyramidal (D_{3h}), or square-pyramidal (C_{4v}) geometries, either two or three transitions are expected in the visible range;[23] however, because of the broadness of the observed spectra, it is not possible to make reliable spectral assignments for the present complexes. In any case, as has been pointed out elsewhere,[24,25] caution should be exercised when one attempts to assign stereochemistries to copper(II) complexes solely on the basis of visible spectra.

For $Cu(O\text{-}en\text{-}N\text{-}tnH_4)Cl_2$ (purple isomer), the shift of the broad spectral envelope to lower wavelengths relative to its position in each of the other corresponding green complexes may reflect the presence of a stronger ligand field. Such a shift would be expected if four nitrogen donor atoms were coordinated to the copper ion rather than the O_2N_2-donor set provided by one macrocycle. This could occur if two nitrogens from each of two ligands coordinated to a single copper ion. For such a case, the purple complex could be formulated as $[Cu(O\text{-}en\text{-}N\text{-}tnH_4)_2][CuCl_4]$ and such a formulation is equally consistent with the analytical and magnetic data for the complex. A structure such as just proposed implies noncoordination of some or all of the ether functions. NMR evidence for noncoordination of the ether groups when $O\text{-}en\text{-}N\text{-}tnH_4$ and other ligands of the present series coordinate to zinc(II) and cadmium(II) has recently been obtained,[26] and such absence of coordination has been confirmed in the solid state for one zinc complex by X-ray diffraction.[26] Noncoordination of ether linkages in a copper complex of the closely related macrocycle **5** containing a potential O_2N_3-donor set



5

has also been observed recently by X-ray diffraction.[27] Similarly there are two other reports,[28,29] both confirmed by

---

[22] Attempts to isolate pure samples of the analogous complexes to $[Cu(O\text{-}en\text{-}N\text{-}tnH_4)Cl]ClO_4$ with **1**, **3**, or **4** were unsuccessful and led to a mixture of products.

[23] Tomlinson, A. A. G.; Hathaway, B. J. *J. Chem. Soc. A* **1968**, 1685.

[24] McKenzie, E. D. *J. Chem. Soc. A* **1970**, 3095.

[25] Lane, L. W.; Taylor, L. T. *J. Coord. Chem.* **1973**, *2*, 295.

[26] Lindoy, L. F.; Lip, H. C.; Smith, R. J.; Tasker, P. A.; Henrick, K.; McPartlin, M. *Inorg. Chem.*, in press.

[27] Adam, K. R.; Lindoy, L. F.; Lip, H. C.; Rea, J. H.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.*, in press.

[28] Herceg, M.; Weiss, R. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 435.

[29] Drew, M. G. B.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1979**, 481.

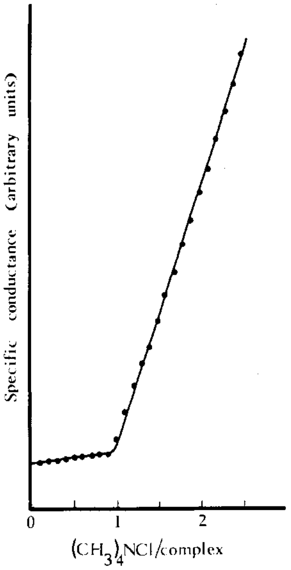


Figure 1. Conductometric titration of Cu(O-en-N-tnH$_4$)(ClO$_4$)$_2$ (10 mL of 1.0 × 10^{-3} M) with [N(CH$_3$)$_4$]Cl (5.0 × 10^{-3} M) in dimethyl sulfoxide.

X-ray studies, of copper compounds of oxygen–nitrogen donor macrocyclic ligands in which ether functions do not coordinate.

Conductance Studies. Conductivity measurements in dimethyl sulfoxide indicate that the diperchlorate complexes are 2:1 electrolytes whereas all of the other complexes have conductances corresponding to 1:1 electrolytes (Table III).[30] Thus the conductance value for the O-en-N-tnH$_4$ complex containing chloride and perchlorate anions is consistent with this complex being five-coordinate in solution. Additional evidence for the formation of five-coordinate species is given by the results of conductometric titrations involving titration of Cu(O-en-N-enH$_4$)(ClO$_4$)$_2$, Cu(O-en-N-tnH$_4$)(ClO$_4$)$_2$, and Cu(O-tn-N-tnH$_4$)(ClO$_4$)$_2$ in dimethyl sulfoxide with tetramethylammonium chloride. In each case a distinct 1:1 end point was obtained which is consistent with the formation of a cation of type [Cu(macrocycle)Cl]$^+$(Figure 1). There was no evidence for coordination of a second chloride ion in any of the titrations. Further, conductance studies suggest that all the dihalide complexes (Table III) are five-coordinate in dimethyl sulfoxide as all had conductances corresponding to 1:1 electrolytes.

From the above studies, it seems unlikely that the purple species, formulated as [Cu(O-en-N-tnH$_4$)$_2$][CuCl$_4$], would dissolve in dimethyl sulfoxide to liberate the complex cation and anion intact, even though this would be consistent with the conductance data. Indeed this purple complex produces a green solution in dimethyl sulfoxide which yields a nearly identical visible spectrum to that of [Cu(O-en-N-tnH$_4$)Cl]ClO$_4$ (Figure 2). Hence, it appears that the purple complex rearranges almost completely in dimethyl sulfoxide to yield a five-coordinate cation of the type discussed above. A similar structure in dimethyl sulfoxide for each of the other dichloride complexes seems likely. In agreement with this, it was found that the visible spectrum of the blue-green complex, Cu(O-en-N-enH$_4$)Cl$_2$·$^1/_2$H$_2$O, was identical with that of a mixture of this complex and its purple analogue in dimethyl sulfoxide (the mixture was isolated as the initial product from the synthetic procedure).

Spectrophotometric Titrations. Spectrophotometric titrations involving incremental addition of O-en-N-tnH$_4$, O-tn-N-tnH$_4$, or O-bn-N-tnH$_4$ to copper perchlorate in dimethyl sulfoxide are consistent with the formation of an initial species with a 1:1 copper to ligand ratio followed by a 1:2 species. In each case an isobestic point was obtained after the addition of one mole ratio of ligand (corresponding to the conversion of the ML^{2+} species to an ML$_2$$^{2+}$ species). The titrations also indicate the gradual formation of a third species at higher ligand concentrations (the formation of this third species was more pronounced for the titration involving O-tn-N-tnH$_4$). The titration curves for the interaction of copper perchlorate with O-en-N-tnH$_4$ are given in Figure 3, and a plot of the formation of the 1:1 and 1:2 (copper to ligand) species derived from these curves is also given (Figure 4). As already mentioned, it was assumed that there is consecutive formation of ML^{2+} and ML$_2$$^{2+}$ species in this system. The percent 1:1 species present was obtained from the variation of absorbance at the wavelength of the isobestic point (630 nm). It was assumed that the absorbance at the isobestic point corresponds to that when 100% ML^{2+} is formed; the respective absorbances at 630 nm thus give estimates of the percent ML^{2+} present (for the initial part of the titration) since the absorbance of copper perchlorate at 630 nm is insignificant.

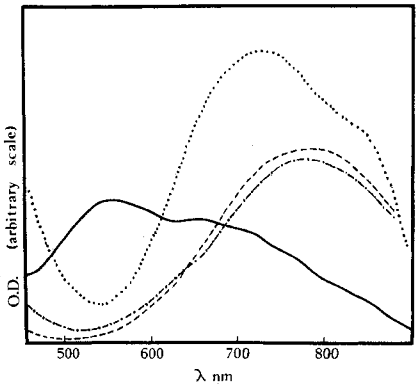


Figure 2. Solid-state and solution (dimethyl sulfoxide) visible spectra. [Cu(O-en-N-tnH$_4$)Cl]ClO$_4$: solid (···), solution (---) (λ_{max} = 795 nm, ϵ = 145 M^{-1} cm^{-1}). [Cu(O-en-N-tnH$_4$)$_2$][CuCl$_4$]: solid (—), solution (-··-).

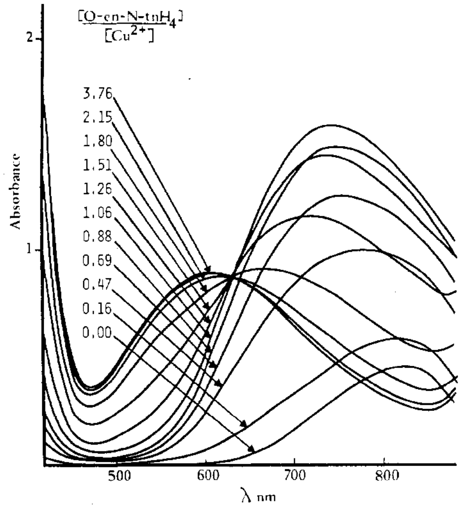


Figure 3. Spectrophotometric titration of copper(II) perchlorate hexahydrate (1.37 × 10^{-2} M) with O-en-N-tnH$_4$ in dimethyl sulfoxide.

Similarly, the absorbances at 490 nm for each titration curve may be taken as a direct approximation of the amount of ML$_2$$^{2+}$ species presence since both the ML^{2+} species and copper perchlorate have insignificant absorption at this wavelength.

Spectrophotometric titration of copper chloride (in dimethyl sulfoxide) with O-en-N-tnH$_4$ initially indicated the formation of an ML^{2+} species, but then, in contrast to the above behavior involving copper perchlorate, there was only a very gradual formation of a second species (with a maximum at a lower wavelength than that of the 1:1 species). The second species was still incompletely formed even when a ligand to metal ratio of approximately 8 had been reached. It is apparent that the

---

[30] Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

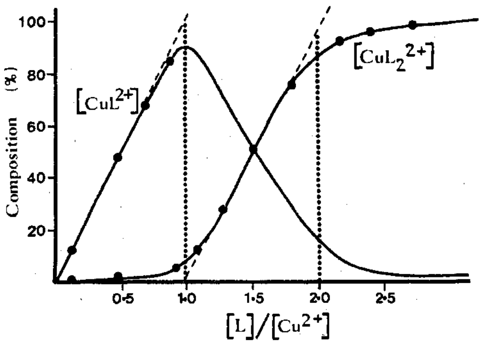


Figure 4. Plot of the formation of the 1:1 and 1:2 (copper to ligand) species for the interaction of O-en-N-tnH_4 with copper perchlorate in dimethyl sulfoxide.

presence of the chloride ion inhibits the formation of this second species having a higher macrocycle to metal ratio than 1:1. In accord with the results discussed earlier, this is probably the result of the formation of a particularly stable five-coordinate species.

The relative positions in the spectrophotometric titrations of the spectral envelopes for the 1:1 and 2:1 complexes are also qualitatively in accord with the structures proposed for these species. As mentioned previously, an N_4-donor set (as postulated for the 2:1 complexes) should cause a shift of the observed absorptions to higher energies when compared with an O_2N_2-donor set. Such a shift was observed for the respective species. This behavior is clearly illustrated in Figure 2 which compares the visible spectrum of the compound formulated as $[Cu(O\text{-en-}N\text{-tn}H_4)_2][CuCl_4]$ in the solid state with the spectrum obtained when this compound is dissolved in dimethyl sulfoxide. For comparison, the spectrum of an authentic sample of $[Cu(O\text{-en-}N\text{-tn}H_4)Cl]ClO_4$ in the solid state and in solution is also given.

NMR Line Broadening Studies. In an attempt to gain further information concerning which donor atoms coordinate, an investigation of the effect of copper ion (chloride and perchlorate salts) on the ^1H NMR spectrum of O-en-N-tnH_4 in Me_2SO-d_6 was undertaken. In each case, moderate concentrations of copper ion led to excessive contact broadening of the resonances, and little information could be extracted from the spectra. However when very low concentrations of copper chloride were present, it was possible to observe the occurrence of much greater broadening of the singlet corresponding to the methylene groups adjacent to the nitrogen donors than for the singlet from the methylene groups adjacent to oxygen (see Figure 5); a similar broadening pattern was obtained with copper perchlorate. Clearly this result supports the inference from the above studies that, in the presence of a large excess of ligand, it is the nitrogen atoms and not the oxygen atoms of the macrocycle that will coordinate to the copper ion.[31]

X-ray Diffraction Study of $[Cu(O\text{-en-}N\text{-tn}H_4)Cl]ClO_4$. In the solid state, the green or green-blue dihalo complexes as well as the chloro–perchlorate complex (Table III) appear from the studies already discussed to be very likely five-coordinate, and such a geometry may also occur in the diperchlorate species. Since it was not possible, from the studies described so far, to predict fine structural details of the complexes postulated to be five-coordinate, an X-ray diffraction study of one such compound, $[Cu(O\text{-en-}N\text{-tn}H_4)Cl]ClO_4$, has been undertaken.

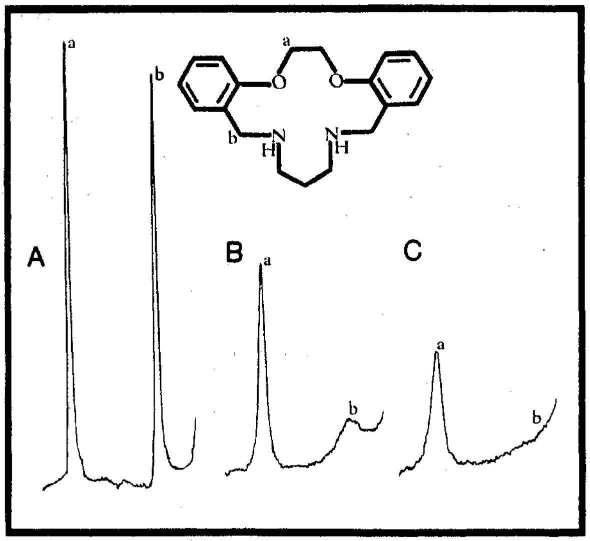


Figure 5. Effect of small additions of copper chloride in Me_2SO-d_6 on the methylene region of the NMR spectrum of O-en-N-tnH_4 (0.104 M) in Me_2SO-d_6: A, $[Cu^{2+}] = 0$; B, $[Cu^{2+}] = 1.85 \times 10^{-3}$ M; C, $[Cu^{2+}] = 3.69 \times 10^{-3}$ M.

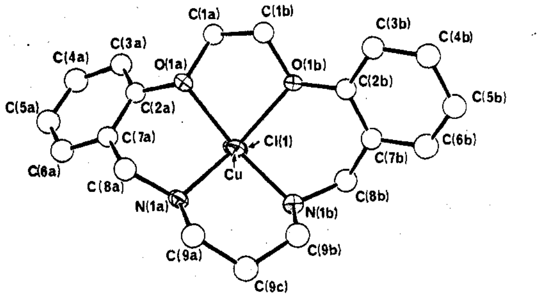


Figure 6. The cation $[Cu(O\text{-en-}N\text{-tn}H_4)Cl]^+$ viewed down the Cu–Cl bond, with atom labels as used in Tables I, II, and IV–VI.

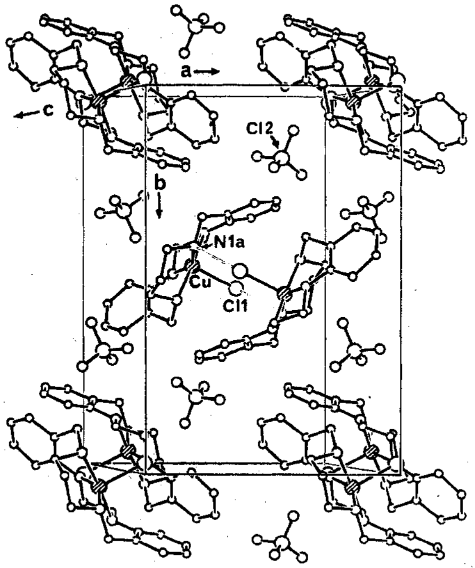


Figure 7. The contents of the unit cell of $[Cu(O\text{-en-}N\text{-tn}H_4)Cl]ClO_4$ viewed down c^*.

A five-coordinate geometry was confirmed for this complex (see Figure 6). The $[Cu(O\text{-en-}N\text{-tn}H_4)Cl]^+$ cations are held together in pairs about an inversion center by weak intermolecular hydrogen bonds between the amino hydrogen atom HN(1a) and the coordinated chloride ion (see Table IV and Figure 7).

Very high thermal parameters for the perchlorate oxygen atoms indicate disorder; attempts to resolve this disorder into sites with partial occupancy were unsuccessful. The oxygen

---

[31] A detailed NMR study of the interaction of this macrocyclic system with a number of paramagnetic metal ions is planned for the future.

Table IV. Shortest Intermolecular Contacts (<2.7 Å) Excluding Interhydrogen Contacts

atoms[a]	dist, Å	atoms[a]	dist, Å
Cl(1) . . . HN(1a)[b]	2.16	Cl(1) . . . H(1b2)[g]	2.51
O(23) . . . H(8b2)[c]	2.39	O(23) . . . H(1b1)[d]	2.56
O(21) . . . H(9a1)[d]	2.40	O(21) . . . H(9b2)[d]	2.59
O(24) . . . H(4a)	2.42	O(22) . . . H(9b1)[b]	2.61
O(22) . . . H(1a2)[e]	2.49	O(21) . . . H(1b1)[d]	2.64
O(24) . . . H(6a)[f]	2.51		

[a] Positional parameters of the first atoms listed are related to those given in Table I by the operations in footnotes *b*–*g*. Hydrogen atoms are assigned the same number as the carbon or nitrogen atom to which they are attached. A final digit indicates that it is one of two H atoms on a methylene carbon. [b] $-x, -y, -z$. [c] $^1/_2 - x, y - {}^1/_2, {}^1/_2 - z$. [d] $x - 1, y, z$. [e] $^1/_2 - x, {}^1/_2 - y, {}^1/_2 + z$. [f] $x - {}^1/_2, {}^1/_2 - y, z - {}^1/_2$. [g] $-x, -y, 1 - z$.

Table V. Interatomic Bond Lengths and Angles

Bond Lengths (Å)			
C(1a)–O(1a)	1.471 (9)	C(1b)–O(1b)	1.467 (8)
O(1a)–C(2a)	1.401 (9)	O(1b)–C(2b)	1.399 (9)
C(2a)–C(3a)	1.38 (1)	C(2b)–C(3b)	1.38 (1)
C(3a)–C(4a)	1.41 (1)	C(3b)–C(4b)	1.38 (1)
C(4a)–C(5a)	1.36 (1)	C(4b)–C(5b)	1.39 (1)
C(5a)–C(6a)	1.35 (1)	C(5b)–C(6b)	1.38 (1)
C(6a)–C(7a)	1.41 (1)	C(6b)–C(7b)	1.40 (1)
C(7a)–C(2a)	1.39 (1)	C(7b)–C(2b)	1.40 (1)
C(7a)–C(8a)	1.48 (1)	C(7b)–C(8b)	1.50 (1)
C(8a)–N(1a)	1.49 (1)	C(8b)–N(1b)	1.51 (1)
N(1a)–C(9a)	1.489 (9)	N(1b)–C(9b)	1.48 (1)
C(9a)–C(9c)	1.51 (1)	C(9b)–C(9c)	1.51 (1)
C(1a)–C(1b)	1.48 (1)	Cu–Cl(1)	2.411 (2)
Cu–O(1a)	2.048 (5)	Cu–O(1b)	2.147 (5)
Cu–N(1a)	1.998 (6)	Cu–N(1b)	1.960 (6)
Cl(2)–O(21)	1.44 (1)	Cl(2)–O(22)	1.32 (1)
Cl(2)–O(23)	1.37 (1)	Cl(2)–O(24)	1.35 (1)
Angles (Deg)			
Cl(1)–Cu–O(1a)	91.4 (1)	Cl(1)–Cu–O(1b)	97.0 (2)
Cl(1)–Cu–N(1a)	111.2 (2)	Cl(1)–Cu–N(1b)	92.2 (2)
O(1a)–Cu–N(1a)	92.0 (2)	O(1b)–Cu–N(1b)	92.3 (2)
O(1b)–Cu–O(1a)	79.8 (2)	N(1a)–Cu–N(1b)	93.7 (3)
O(1b)–Cu–N(1a)	150.8 (2)	O(1a)–Cu–N(1b)	171.7 (2)
C(1b)–C(1a)–O(1a)	106.3 (6)	C(1a)–C(1b)–O(1b)	106.7 (6)
C(1a)–O(1a)–C(2a)	116.9 (5)	C(1b)–O(1b)–C(2b)	118.2 (5)
C(1a)–O(1a)–Cu	109.2 (4)	C(1b)–O(1b)–Cu	109.0 (4)
C(2a)–O(1a)–Cu	113.0 (4)	C(2b)–O(1b)–Cu	123.7 (4)
O(1a)–C(2a)–C(3a)	123.5 (7)	O(1b)–C(2b)–C(3b)	123.0 (7)
O(1a)–C(2a)–C(7a)	113.4 (6)	O(1b)–C(2b)–C(7b)	115.4 (7)
C(3a)–C(2a)–C(7a)	123.1 (8)	C(3b)–C(2b)–C(7b)	121.5 (7)
C(2a)–C(3a)–C(4a)	119.0 (8)	C(2b)–C(3b)–C(4b)	119.6 (8)
C(3a)–C(4a)–C(5a)	118.1 (9)	C(3b)–C(4b)–C(5b)	120.2 (9)
C(4a)–C(5a)–C(6a)	122.8 (9)	C(4b)–C(5b)–C(6b)	119.9 (9)
C(5a)–C(6a)–C(7a)	121.2 (8)	C(5b)–C(6b)–C(7b)	121.1 (9)
C(6a)–C(7a)–C(2a)	115.7 (7)	C(6b)–C(7b)–C(2b)	117.6 (8)
C(6a)–C(7a)–C(8a)	122.8 (7)	C(6b)–C(7b)–C(8b)	119.0 (7)
C(2a)–C(7a)–C(8a)	121.5 (7)	C(2b)–C(7b)–C(8b)	123.0 (7)
C(7a)–C(8a)–N(1a)	112.4 (7)	C(7b)–C(8b)–N(1b)	114.1 (7)
C(8a)–N(1a)–C(9a)	111.2 (6)	C(8b)–N(1b)–C(9b)	113.1 (6)
C(8a)–N(1a)–Cu	112.4 (5)	C(8b)–N(1b)–Cu	111.1 (5)
C(9a)–N(1a)–Cu	116.9 (5)	C(9b)–N(1b)–Cu	115.4 (5)
N(1a)–C(9a)–C(9c)	112.9 (7)	N(1b)–C(9b)–C(9c)	110.2 (7)
C(9a)–C(9c)–C(9b)	116.0 (8)	O(21)–Cl(2)–O(22)	109 (1)
O(21)–Cl(2)–O(23)	108 (1)	O(21)–Cl(2)–O(24)	108 (1)
O(22)–Cl(2)–O(23)	115 (1)	O(22)–Cl(2)–O(24)	105 (1)
O(23)–Cl(2)–O(24)	112 (1)		

atoms show no particularly short intermolecular contacts (Table IV), and this is in accord with the infrared data (see previous discussion) which provide no evidence for lowering of T_d symmetry due to packing effects, H bonding, or metal coordination.

The irregular coordination polyhedron about the copper ion approximates most closely to a trigonal bipyramid with the O(1a) and N(1b) atoms occupying the axial sites (Figure 8). A nonequivalence of the Cu–N bonds would be expected in such an arrangement; the observed values (Table V) do differ significantly, but both fall within the range of values (1.88–2.24 Å) reported[32] for five-coordinate copper(II) complexes which have "ClN_xO_{4-x}" donor sets.[33] Similarly, the observed Cu–Cl length falls centrally in the range (2.11–2.64 Å) of values[32] found for related five-coordinated complexes.

The Cu–O distances in [Cu(O-en-N-tnH$_4$)Cl]$^+$ are short in comparison with other copper(II)–ether complexes (Table VI) which show a considerable range (2.11–2.75 Å) of values—often[34] larger than the sum of the respective covalent

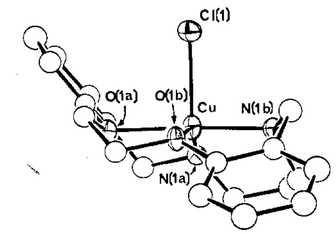


Figure 8. The folding of the macrocycle in the cation [Cu(O-en-N-tnH$_4$)Cl]$^+$.

Table VI. Bond Lengths and Angles at Oxygen in Copper(II)–Ether Complexes[a]

Cu–O, Å	Cu–O–C, deg		C–O–C, deg	ref
2.05	109	113	117	this work
2.11	112	112	114	*b*
2.13	116	119	112	*b*
2.13	112	130	115	*c*
2.15	109	124	118	this work
2.31	108	133	118	*d*
2.32	108	132	119	*e*
2.34	102	112	114	*b*
2.37	107	131	113	*f*
2.39	108	132	114	*g*
2.40	103	112	115	*b*
2.41	104	128	118	*e*
2.43	107	135	117	*c*
2.49	103	138	117	*h*
2.50	106	135	117	*c*
2.56	100	140	116	*i*
2.57	102	141	117	*h*
2.71	96	125	110	*j*
2.75	96	121	112	*j*

[a] Calculated from atomic parameters in the Cambridge Crystallographic Data Centre files using the CSSR programs (see ref 32). [b] Van Remoortere, F. P.; Boer, F. P.; Steiner, E. C. *Acta Crystallogr., Sect. B* 1975, *B31*, 1420. [c] Prout, C. K.; Armstrong, R. A.; Carruthers, J. R.; Forrest, J. G.; Murray-Rust, P.; Rossotti, F. J. C. *J. Chem. Soc. A* 1968, 2791. [d] Greenhough, T. J.; Ladd, M. F. C. *Acta Crystallogr., Sect. B* 1978, *B34*, 2744. [e] Hobson, R. J.; Ladd, M. F. C.; Povey, D. C. *J. Cryst. Mol. Struct.* 1973, *3*, 377. [f] Prout, C. K.; Barrow, M. J.; Rossotti, F. J. C., *J. Chem. Soc. A* 1971, 3326. [g] Prout, C. K.; Carruthers, J. R.; Rossotti, F. J. C. *Ibid.* 1971, 554. [h] Greenhough, T. J.; Ladd, M. F. C. *Acta Crystallogr., Sect. B* 1978, *B34*, 2619. [i] Ladd, M. F. C.; Povey, D. C. *J. Cryst. Mol. Struct.* 1976, *6*, 205. [j] Herceg, M.; Weiss, R. *Acta Crystallogr., Sect. B* 1973, *B29*, 542.

---

(32) Neitzel, C. J.; Desiderato, R. *Cryst. Struct. Commun.* **1975**, *4*, 333. De Meester, P.; Skapski, A. C. *J. Chem. Soc. A* **1971**, 2167. Stephens, F. S.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2293. Laskowski, E. J.; Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 2449. Caira, M. R.; Nassimbeni, L. R.; Woolley, P. R. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1334. Bertrand, J. A.; Kelly, J. A.; Breece, J. L. *Inorg. Chim. Acta* **1970**, *4*, 247. Hoskins, B. F.; McLeod, N. J.; Schaap, H. A. *Aust. J. Chem.* **1976**, *29*, 515. Udupa, M. R.; Krebs, B. *Inorg. Chim. Acta* **1979**, *32*, 1.

(33) References were retrieved from a search of the Cambridge Crystallographic Data Centre Files, accessed via the CSSR program (Elder, M.; Machin, P.; Mills, O S. "CSSR"; Daresbury Research Laboratory, Science Research Council: Warrington, U.K., 1977).

(34) Bullock, J. I.; Ladd, M. F. C.; Povey, D. C. *J. Chem. Soc., Dalton Trans.* **1977**, 2242.

radii. In many of these complexes the two Cu–O–C angles for uncoordinated ether oxygen differ considerably, and, in general, the longer Cu–O bonds are observed in the complexes in which this difference is large (Table VI). A weaker Cu–O bond would be expected in such cases because the copper atom will not be in the plane through the oxygen atom which contains the two sp^3 lone pairs (in an sp^3 model for the oxygen atom) or the sp^2 pair (for an sp^2 model).[35] In accordance with this, in $[Cu(O\text{-en-N-tnH}_4)Cl]^+$ the shorter Cu–O distance is observed for the oxygen, O(1a), which shows the more nearly tetrahedral bond angles (Table V).

The agreement is good between chemically equivalent bond lengths and angles in the two halves of the macrocycle (Table V), and the values are similar to those observed[10] in the octahedral nickel(II) complex $[Ni(O\text{-en-N-tnH}_4)Cl_2]$.

The configuration of the ligand differs considerably in the five-coordinate copper(II) and six-coordinate nickel(II) complexes. In the latter[10] the ligand presents an almost planar O_2N_2-donor set, and the two benzyl chelate rings are bent down almost equally (13 and 11° for rings A and B) to the same side of the O_2N_2 plane. In the copper complex $[Cu(O\text{-en-N-tnH}_4)Cl]^+$ the O_2N_2-donor set is much less planar with atoms showing "tetrahedral" displacements of ±0.22 Å. The benzyl chelate rings are both inclined at 21° to the best plane through the O_2N_2-donor set but in this complex are bent to opposite sides of this plane (a comparison of atom deviations from selected least-squares planes in the copper and nickel complexes of macrocycle **2** together with the angles between these planes is given in Table iv of the supplementary material).

Despite these differences in ligand conformation, the radii[36] of the holes defined by the donor atoms in the nickel(II) and copper(II) complexes are similar (2.09 and 2.01 Å, respectively). The corresponding values found[37] in the free ligand in two different conformations in the solid state are 2.09 and 2.15 Å. The importance of variations in hole size of ligands **1–4** in controlling stability of the complexes with copper(II) will be limited by the fact that in five-coordinate complexes the metal ion is not located inside the ligand at the centroid of the donor set. Thus in $[Cu(O\text{-en-N-tnH}_4)Cl]^+$ the copper atom is displaced 0.29 Å from the best plane through the O_2N_2 donors toward the chlorine atom.

Stability Constant Determinations. Stability constants for the copper complexes in 95% methanol have been obtained by the pH titration procedure under the same conditions [$I = 0.1$, $(CH_3)_4NCl$] to those used previously for the analogous nickel complexes. Unlike the interaction of copper(II) with tetraaza macrocycles which can require several months to reach equilibrium in the presence of acid,[38] equilibrium for the present O_2N_2-donor systems was reached moderately quickly (typically, in less than 10 min). log K values corresponding to equilibrium 2 were obtained.

$$M^{2+} + L \overset{K}{\rightleftharpoons} ML^{2+} \qquad K = [ML^{2+}]/[M^{2+}][L] \qquad (2)$$

It was not possible in these determinations to obtain complete titration curves because of either complex precipitation or competing metal ion hydrolysis The titration data for the copper(II) complexes were refined satisfactorily on the assumption that the presence of a 1:1 metal to ligand species and no improvement occurred when other species were included. As already discussed the presence of chloride ion in the background electrolyte should promote the formation of $[CuLCl]^+$ species relative to species having higher ligand to copper ratios. If species having ligand to metal ratios other than 1:1 do form, it is apparent that they are insignificant for the range of $\bar{n}$ values encountered in the present studies.

Table VII. log of Stability Constants for Copper(II) and Nickel(II) Complexes of the O_2N_2-Donor Macrocycles[a]

ligand	ring size	log K for $M^{2+} + L \rightleftharpoons ML^{2+}$	
		Ni(II)[b]	Cu(II)
O-en-N-enH_4	14	3.7 ± 0.2[c]	8.2 ± 0.1
O-en-N-tnH_4[d]	15	5.4 ± 0.1	7.2 ± 0.1
O-tn-N-tnH_4	16	5.8 ± 0.1	7.7 ± 0.1
O-bn-N-tnH_4	17	3.5 ± 0.3	7.2 ± 0.2

[a] In 95% methanol [$I = 0.1$, $(CH_3)_4NCl$] at 25 °C. [b] Nickel log K values from ref 18. [c] Errors represent three standard deviations. [d] The corresponding values for the dichloro derivative of this ligand derived from 5-chlorosalicylaldehyde are log $K(Ni(II)) = 4.8 \pm 0.1$ and log $K(Cu(II)) = 6.8 \pm 0.1$.

Table VIII. Kinetic Data for Dissociation of the Copper Complexes in 95% Methanol

ligand	ring size	[HCl], M	$k_{obsd}{}^{25}$,[a,b] s^{-1}
1	14	0.1	(1.6 ± 0.1) × 10
1	14	0.05[c]	(1.5 ± 0.1) × 10
2	15	0.1	$>10^2$ [d]
3	16	0.1	$>10^2$ [d]
4	17	0.1	(8.5 ± 2.0) × 10

[a] Errors are three standard deviations. [b] Complex concentrations: 10^{-2}–10^{-3} M. [c] Ionic strength = 0.1, $(CH_3)_4NCl$. [d] Too fast to obtain a value by the stopped-flow method.

The log K values obtained for the copper(II) complexes are listed in Table VII together with those obtained previously (under similar conditions) for nickel(II) with the same ligands.[9,18] The copper complexes show no definite peak in stability along the ligand series. The lack of a distinct ring-size discrimination effect for copper very likely reflects that the respective macrocycles do not completely encircle the copper ion in these complexes; as just discussed, the X-ray structure of $[Cu(O\text{-en-N-tnH}_4)Cl]ClO_4$ shows that the copper ion sits slightly above the hole of the macrocycle. In contrast to the above behavior, the interaction of **1–4** with nickel provides a clear example of macrocyclic ring-size control of thermodynamic stability, and the X-ray diffraction studies[9,10] confirm that the respective nickel ions are contained in the plane of the O_2N_2-donor sets in the complexes of the 15- and 16-membered cyclic ligands.

The absence of a well-defined ring-size effect in the present series of copper complexes parallels that observed recently for the copper complexes of a series of related S_4-donor macrocycles.[39] Nevertheless for a number of N_4-donor macrocycles, evidence for ring-size discrimination toward copper(II) (residing largely in enthalpic effects) has been presented.[40,41] However, in the absence of confirmation that a common stereochemistry is maintained along each of these series of copper complexes, it would seem that caution needs to be exercised in any attempted direct correlation of macrocycle

---

(35) In cyclic polyether complexes the alkali metal ion to oxygen bond axes frequently do not align with the predicted orientation of lone pairs on the oxygen atoms (Mercer, M.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2215), and there is little correlation between metal–oxygen distances and the geometry at the oxygen atoms (Truter, M. R., personal communication).

(36) Calculated as the mean distance of the donor atoms from their centroid. The individual distances (angstroms) for the nickel(II) complex are as follows: O(1a), 2.065; O(1b), 1.974; N(1a), 2.165; N(1b), 2.157. Distances (angstroms) for the copper(II) complex are as follows: O(1a), 1.966; O(1b), 1.995; N(1a), 2.042; N(1b), 2.054.

(37) Lindoy, L. F.; Tasker, P. A.; Trotter, J., submitted for publication.

(38) Hinz, F. P.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2941.

(39) Diaddario, L. L.; Zimmer, L. L.; Jones, T. E.; Sokol, L. S. W. L.; Cruz, R. B.; Yell, E. L.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1979**, *101*, 3511.

(40) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *J. Chem. Soc., Dalton Trans.* **1978**, 577.

(41) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1978**, 1081.

Table IX. Ratio of $k(\mathrm{Cu})/k(\mathrm{Ni})$ for ML^{2+} in 0.1 M HCl[a]

	ligand			
	1	2	3	4
ring size	14	15	16	17
$k(\mathrm{Cu})/k(\mathrm{Ni})$	2.3	$>8.8 \times 10^3$	$>1.9 \times 10^4$	$>1.7 \times 10^2$

[a] In 95% methanol at 25 °C.

ligand hole size with observed thermodynamic trends.

Kinetics of Dissociation. The kinetics of dissociation of the copper complexes in 95% methanol containing HCl ($I = 0.1$) have been studied. Table VIII lists the first-order rate data obtained when the dissociation of these complexes was followed in 0.1 M HCl as well as the rate for the complex of O-en-N-enH$_4$ in 0.05 M HCl; for this latter complex there is no significant difference between the observed rate constants for the two acid concentrations. A similar independence of acid concentration was observed for the dissociation of the corresponding complexes of nickel(II) both in 95% methanol and in aqueous media.[8] In all these cases it appears that the function of the acid is to scavenge the free ligand once it has dissociated from the copper ion (eq 3).

$$\begin{aligned} \mathrm{CuL^{2+}} &\rightarrow \mathrm{Cu^{2+}} + \mathrm{L} \quad \text{(rate determining)} \\ \mathrm{L} + 2\mathrm{H^+} &\rightarrow \mathrm{LH_2^{2+}} \quad \text{(fast)} \end{aligned} \tag{3}$$

Comparison of the dissociation rates for the nickel and copper complexes of macrocycles **1**–**4** (Table VIII) reveals a striking example of kinetic discrimination between these metal ions. Specifically, for the 16-membered macrocycle, the dissociation rate of its copper complex is more than 1.9×10^4 times greater than that of its nickel complex, while for the 14- and 17-membered macrocycles it is only 2.3 and <170 times greater, respectively. Such discriminating ability undoubtedly reflects a number of factors, including the difference in covalent radii of the two ions and the likelihood that the copper ion sits out of the hole of the respective cyclic ligands—as discussed above for [Cu(O-en-N-tnH$_4$)Cl]ClO$_4$ in the solid state. Although some limited examples of related kinetic selectivity involving alkali and alkaline earth complexes of polyether-type macrocycles have been observed,[42] evidence for discrimination behavior of the type shown in Table IX involving different transition-metal ions has been quite rare.[5] Such data provide the foundation for the development of highly selective chromatography materials (macrocycles attached to insoluble supports) for transition-metal ions. Further work in this area is proceeding.

Acknowledgment. L.F.L. expresses thanks to the ETH, Zürich, for support during a period spent at the Laboratorium für Anorganische Chemie. Acknowledgment is made to the Australian Research Grants Committee for support and to the Australian Institute of Nuclear Science and Engineering for a travel grant. We wish to thank Dr. A. Ekstrom (Atomic Energy Commission, Sydney), Mr. B. Rüttimann (ETH, Zürich), and Dr. J. T. Baker (Roche Research Institute of Marine Pharmacology, Sydney) for assistance. M.M. and P.A.T. thank the Science Research Council (Warrington, U.K.) for diffractometer equipment and computing facilities.

Registry No. **1**, 65639-47-6; **2**, 65639-43-2; **3**, 65639-49-8; **4**, 66793-29-1; Cu(O-en-N-enH$_4$)(ClO$_4$)$_2$, 74261-95-3; Cu(O-en-N-enH$_4$)Cl$_2$, 74261-96-4; Cu(O-en-N-tnH$_4$)(ClO$_4$)$_2$, 74261-98-6; [Cu(O-en-N-tnH$_4$)Cl]ClO$_4$, 74262-00-3; Cu(O-en-N-tnH$_4$)Cl$_2$, 74310-47-7; Cu(O-tn-N-tnH$_4$)(ClO$_4$)$_2$, 74282-40-9; Cu(O-tn-N-tnH$_4$)Cl$_2$, 74262-01-4; Cu(O-bn-N-tnH$_4$)Cl$_2$, 74262-02-5; Cu(O-bn-N-tnH$_4$)Br$_2$, 74262-03-6; Ni(O-en-N-tnH$_4$)Cl$_2$, 66810-83-1; [Cu(O-en-N-tnH$_4$)$_2$][CuCl$_4$], 74262-05-8.

Supplementary Material Available: Listings of analytical data, full thermodynamic and kinetic data, a comparison of least-squares planes in the copper and nickel structures of macrocycle **2**, and structure factor tables for the copper complex are available (16 pages). Ordering information is given on any current masthead page.

---

(42) Cox, B. G.; Schneider, H. *J. Am. Chem. Soc.* **1977**, *99*, 2809. Cox, B. G.; Schneider, H.; Stroka, J. *Ibid.* **1978**, *100*, 4746.

Contribution from the Webster Research Center,
Xerox Corporation, Webster, New York 14580

Crystal and Molecular Structure of Unsolvated Triphenyltelluronium Chloride, $(C_6H_5)_3TeCl$

RONALD F. ZIOLO* and MICHAEL EXTINE[1]

Received February 13, 1980

The structure of unsolvated triphenyltelluronium chloride, $(C_6H_5)_3TeCl$, has been determined by a single-crystal X-ray diffraction study. The salt crystallizes in the space group $P2_1/n$ of the monoclinic system with eight $(C_6H_5)_3TeCl$ units per cell. Lattice parameters (23 ± 1° C) are $a = 11.194$ (2) Å, b 13.381 (2) Å, $c = 21.501$ (3) Å, $\beta = 104.51$ (1)°, and $V = 3117.8$ Å^3. The structure was solved by direct and Fourier methods from automatic diffractometer data collected on an Enraf-Nonius CAD4 using Mo Kα radiation filtered by a graphite-crystal incident-beam monochromator. Refinement by the full-matrix least-squares technique led to a conventional R factor (on F) of 0.023 for 6719 reflections having $F_o^2 > 3\sigma(F_o^2)$. Anisotropic thermal motion was assumed for the nonhydrogen atoms. Triphenyltelluronium chloride is dimeric and predominantly ionic in the solid state. Each tellurium atom is five-coordinate in a distorted square-pyramidal geometry. Two such square pyramids sharing a common basal edge through the bridging chloride ions compose the dimer. The dihedral angle between the pyramid bases is 129° and the axial Te–C vectors point in opposing directions. The Te–C distances are normal and have a mean value of 2.130 (4) Å. The Te–Cl interactions range from 3.142 (1) to 3.234 (1) Å, and the Cl–Te–Cl angles are 90.84 (2) and 92.28 (2)°. Two solvated compounds of the chloride have been identified, $(C_6H_5)_3TeCl\cdot{}^1/_2(C_2H_5)_2O$ and $(C_6H_5)_3TeCl\cdot{}^1/_2C_6H_6$, and unit cell data determined.

Introduction

Recent studies on the triorganochalcogenonium salts, R_3MX, have shown that the salts have relatively complex structures due to weak bonding interactions between the chalcogen atom and the anion.[2-8] It has become evident that these interactions determine the overall structural features of

---

(1) Molecular Structure Corp., 3304 Longmire Dr., College Station, Texas 77840.

(2) Einstein, F.; Trotter, J.; Williston, C. *J. Chem. Soc. A* **1967**, 2018.

(3) Ziolo, R. F.; Pritchett, K. *J. Organomet. Chem.* **1976**, *116*, 211.

(4) Titus, D. D.; Lee, J.-S.; Ziolo, R. F. *J. Organomet. Chem.* **1976**, *120*, 381.

(5) Lee, J.-S.; Titus, D. D. *J. Cryst. Mol. Struct.* **1976**, *6*, 279.