Inorganica Chimica Acta, 58 (1982) 27–33

Versatility of the Cyclic Ligand 5,8,11-Trioxa-2,14-Dithia[15](2,6)-pyridinophane: Crystal and Molecular Structures of its Complexes with Barium Isothiocyanate and with Copper(II) Chloride

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Received July 21, 1981

Colourless crystals of the Ba complex (1), $C_{15}H_{23}NO_3S_2\cdot Ba(SCN)_2\cdot H_2O$, M_r = *601.0, are triclinic,* $P\bar{1}$, a = *9.449(3),* b = *14.710(4),* c = *10.090(4)* Å, α = *113.41(6),* β = *106.89(7),* γ = *74.15(6)°,* Z = *2,* D_c = *1.647,* D_o = *1.65 g cm*$^{-3}$. *The structure was refined to* R = *0.054 for 5565 independent diffractometer data. Dark green needles of the Cu complex (2),* $C_{15}H_{23}NO_3S_2\cdot CuCl_2$, M_r = *463.9, are also triclinic,* $P\bar{1}$, a = *7.912(4),* b = *8.793(5),* c = *15.082(7)* Å, α = *92.79(9),* β = *101.75(8),* γ = *66.56(9)°,* Z = *2,* D_c = *1.636,* D_o = *1.615 g cm*$^{-3}$. *This structure was refined to* R = *0.095 using 2954 unique data.*

As is reflected by torsion angles, there is significantly more ring strain in the complexation of the 'non-fitting' cation Cu^{2+} *than in the complexation of the 'ideal-fitting'* Ba^{2+} *cation. The latter is held in the centre of the cavity of the ligand and nine-fold coordinated to all the six hetero atoms of the ligand, to one water molecule, and to two* ^{-}NCS *anions. With the much smaller* Cu^{2+} *cation, however, the ligand adopts a folded conformation leaving the* Cu^{2+} *coordination geometry relatively undistorted from a regular square pyramid. This is formed by the three neighbouring hetero atoms S, N, S of the ligand and two* Cl^- *anions; oxygen atoms of the ligand are not involved in obvious interactions.*

Introduction

The ratio of the inner diameter of a crown ether to the diameter of a ligated alkali or alkaline earth metal cation can be responsible for the stability [1] as well as for the configuration [2] of a complex. The coordination of a cation fitting the cavity of a macrocyclic ligand offers no problem sterically: the cation is enclosed in the centre of the cavity and is approximately co-planar with the hetero atoms [2, 3]. Cations with radii much bigger than the radius of the cavity are located above the plane of oxygen atoms [2, 4] and sometimes form sandwich or dimeric complexes [2, 5]. However, cations with smaller radii are often cradled but not enclosed by the ligand [6], or give rise to binuclear complexes [7]. Normally, in all three cases all hetero atoms are involved in coordination.

Though complexes of crown ethers with transition metals are known [8, 9], substitution of O by N or S in the ligand seems to improve the coordination abilities towards these cations [9]. The title ligand 5,8,11-trioxa-2,14-dithia[15](2,6)-pyridinophane (nomenclature according to [10]) may be considered as a hetero analogue of 18-crown-6 and contains mixed donor atoms (see Fig. 1). It is, therefore, able to form stable crystalline complexes with alkali, alkaline earth and transition metal cations [11]. The cations Ba^{2+} and Cu^{2+} differ substantially, not only in their radii (1.34 and 0.72 Å [12]) but also in their coordination behaviour: copper usually requires a quite regular coordination geometry [13] whilst alkali and alkaline earth metals can be wrapped in various ways [14]. It therefore seemed worthwhile to investigate the structures of two complexes of the title ligand with $Ba(SCN)_2$ and with $CuCl_2$.

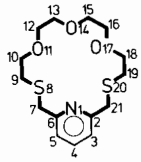

Fig. 1. The chemical structure of 5,8,11-trioxa-2,14-dithia-[15](2,6)-pyridinophane and the numbering scheme adopted in this study.

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*These structures have been reported briefly at the 5th European Crystallographic Meeting, August 1979; in Copenhagen, Denmark.

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Experimental

Crystal Data and Intensities

Colourless chunks of the barium complex *1* and dark green needles of the copper complex *2* were grown from an 1:1 mixture of ethyl acetate and methanol [11]. Preliminary Weissenberg photographs of both compounds revealed no systematic absences and showed triclinic symmetries.

Unit cell dimensions were obtained by a least-squares fit to the settings of 10 high-order reflections on an automated STOE four-circle diffractometer using graphite-monochromated Mo Kα radiation, λ = 0.7107 Å, for *1* and Ni-filtered Cu Kα radiation, λ = 1.5418 Å, for *2*.

1, barium 5,8,11-trioxa-2,14-dithia[15](2,6)-pyridinophane isothiocyanate hydrate, $C_{15}H_{23}NO_3S_2 \cdot Ba(SCN)_2 \cdot H_2O$, M_r = 601.0, triclinic $P\bar{1}$, a = 9.449 (3), b = 14.710(4), c = 10.090(4) Å, α = 113.41(6), β = 106.89(7), γ = 74.15(6)°, U = 1211.6 Å^3, Z = 2, D_c = 1.647, D_o = 1.65 g cm^{-3} (flotation in bromobenzene/ethyl acetate), μ(Mo Kα) = 2.044 mm^{-1}, F(000) = 599. The cell given above can be converted to the standard reduced setting (9.449, 10.090, 14.151 Å, 107.46, 94.40, 106.89°) by application of the matrix 1,0,0, 0,0,1, 0,−1,−1.

A crystal with dimensions *ca.* 0.4 × 0.4 × 0.4 mm^3 was used for collecting intensities of 5565 unique reflections in the $2\theta-\theta$ step scan mode up to 2θ = 60° with a scan time about two times longer than the total background time. Three standards were monitored every 100 reflections, and data were corrected for crystal decay and for Lorentz and polarization effects.

2, copper 5,8,11-trioxa-2,14-dithia[15](2,6)-pyridinophane dichloride, $C_{15}H_{23}NO_3S_2 \cdot CuCl_2$, M_r = 463.9, triclinic $P\bar{1}$, a = 7.912(4), b = 8.793(5), c = 15.082(7) Å, α = 92.79(9), β = 101.75(8), γ = 66.56(9)°, U = 941.9 Å^3, Z = 2, D_c = 1.636, D_o = 1.615 g cm^{-3} (flotation in bromobenzene/ethyl acetate), μ(Cu Kα) = 6.376 mm^{-1}, F(000) = 478. This cell can be converted to the standard setting (7.912, 8.793, 15.082 Å, 87.21, 78.25, 66.56°) by application of the matrix −1,0,0, 0,−1,0, 0,0,1.

TABLE I. Fractional Coordinates (× 10^4) and Anisotropic Temperature Factors (Å^2 × 10^4) (except for H atoms) in the Ba^{2+} Complex. The temperature factor exponent takes the form $-2\pi^2(U_{11}h^2a^{*2} + .. + 2U_{12}hka^*b^*)$.

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba	8154(1)	7652(1)	2463(1)	355(2)	376(2)	309(2)	159(1)	114(1)	−78(1)
N(1)	8040(6)	6329(4)	4079(6)	416(27)	433(28)	403(27)	226(23)	140(22)	−76(22)
C(2)	7659(7)	5409(5)	3342(8)	435(32)	456(34)	551(40)	238(30)	207(29)	−70(26)
C(3)	7727(9)	4766(5)	4078(10)	675(47)	407(37)	867(57)	319(38)	425(43)	−7(33)
C(4)	8184(10)	5079(6)	5581(10)	830(56)	555(43)	804(57)	444(42)	447(47)	37(39)
C(5)	8557(9)	6012(6)	6351(8)	637(46)	695(47)	599(43)	450(39)	349(37)	112(37)
C(6)	8471(7)	6626(5)	5543(7)	432(33)	519(35)	416(32)	268(28)	205(27)	−10(27)
C(7)	8919(9)	7643(5)	6334(7)	656(51)	562(39)	327(32)	175(28)	132(33)	−181(36)
S(8)	7492(2)	8597(1)	5822(2)	565(10)	452(9)	428(9)	136(7)	188(7)	−101(7)
C(9)	8570(10)	9595(6)	6348(8)	866(58)	477(40)	507(41)	75(33)	104(39)	−318(39)
C(10)	7763(11)	10281(6)	5486(10)	1036(70)	408(39)	573(51)	57(36)	297(49)	−166(42)
O(11)	7839(6)	9767(4)	3975(6)	742(34)	382(25)	564(29)	163(22)	196(25)	−80(23)
C(12)	6987(11)	10386(6)	3074(10)	856(60)	476(41)	769(59)	334(41)	271(48)	23(39)
C(13)	7257(10)	9883(6)	1584(10)	800(55)	572(46)	771(56)	416(43)	286(45)	−46(40)
O(14)	6624(6)	8974(4)	907(5)	604(29)	652(31)	466(26)	329(24)	225(22)	−17(24)
C(15)	6663(9)	8509(7)	−627(8)	567(42)	938(60)	456(39)	438(42)	193(33)	29(40)
C(16)	5945(9)	7588(8)	−1253(8)	440(40)	1051(70)	369(35)	295(41)	101(30)	23(42)
O(17)	6896(5)	6834(4)	−632(5)	445(25)	801(35)	362(23)	203(23)	70(19)	−149(24)
C(18)	6265(9)	5936(7)	−1186(8)	524(41)	993(64)	358(34)	62(37)	95(30)	−298(42)
C(19)	7469(10)	5071(7)	−969(8)	647(49)	692(51)	404(36)	−54(34)	188(34)	−217(41)
S(20)	8504(2)	5234(1)	893(2)	514(9)	482(9)	435(9)	49(7)	196(7)	−140(7)
C(21)	7117(8)	5119(5)	1727(8)	633(42)	494(39)	583(42)	121(33)	198(34)	−272(33)
S(22)	14231(2)	6824(2)	4479(2)	414(9)	661(12)	530(10)	193(9)	124(8)	−38(8)
C(23)	12393(7)	7140(5)	4231(6)	487(37)	367(30)	345(29)	163(24)	101(25)	−101(26)
N(24)	11103(6)	7354(5)	4065(7)	429(31)	619(38)	621(38)	331(32)	114(27)	−82(27)
S(25)	12200(3)	8017(3)	−270(3)	581(13)	1710(30)	810(16)	730(19)	184(11)	−313(16)
C(26)	11005(7)	7897(5)	500(7)	406(32)	627(41)	462(34)	249(31)	139(27)	−60(29)
N(27)	10146(8)	7816(6)	1015(9)	585(39)	1143(60)	830(49)	540(45)	316(36)	−127(38)
O(28)	5174(6)	7638(5)	2217(7)	455(29)	1345(51)	747(37)	614(36)	147(26)	−156(31)
H(1)	4345(16)	7602(15)	1527(16)	504(67)					
H(2)	4824(16)	7457(15)	2823(16)	506(67)					

Intensities for 2954 unique reflections were collected from a crystal with dimensions *ca.* 0.1 × 0.2 × 0.6 mm^3 in the $2\theta-\theta$ step scan mode up to $\sin\theta = 0.8725$ with a scan time of about three times the total background time. Three standards were monitored every 100 reflections and data were corrected for crystal decay and for Lorentz effects.

Structure Determinations

The following programs were used on the Univac 1108 computer of the Gesellschaft für wissenschaftliche Datenverarbeitung, Göttingen: MULTAN 77 [15] for direct methods, SHELX 76 [16] for Patterson syntheses and structure refinement, and ORTEP [17] for producing figures.

1: The position of Ba^{2+} was taken from an ExF Patterson map; subsequent Fourier syntheses yielded the positions of all remaining non-hydrogen atoms. Anisotropic blocked-matrix least-squares refinement of these atoms minimised $\Sigma w|\Delta|^2$ with $w = 1/\sigma^2(F_o)$; all H atoms could then be located from a difference Fourier map. Their positions were recalculated from the carbon skeleton with C–H = 1.08 Å and U = 0.05 Å^2 and kept in ideal positions in further refinement; only parameters of water H atoms were allowed to vary during the last cycle (with a damping factor).

The highest residual electron density in the final difference map was 0.95 electrons per Å^3 close to the heavy atom. Mean values of $w\cdot\Delta^2$ showed virtually no dependence on $\sin\theta$. Convergence was achieved at $R = \Sigma\Delta/\Sigma F_o = 0.053$ and $R_w = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}F_o = 0.050$ where $\Delta = |F_o| - |F_c|$ and $w = 1/\sigma^2(F_o)$.

2: The structure was solved by direct methods followed by Fourier syntheses, and refined anisotropically by blocked-matrix least-squares methods. H atoms were placed in ideal positions (C–H distances 1.08 Å) with U = 0.05 Å^2. The last difference map showed a maximum residual electron density of 0.73 e/Å^3, mean values of $w\Delta^2$ were virtually independent of $\sin\theta$. Final values of R and R_w were 0.095 and 0.090 respectively, with all data included.

Refined atom parameters are given in Tables I and II, the numbering scheme adopted may be taken from Fig. 1. Because of the (non-crystallographic) mirror plane through C(4), N(1) and O(14) (see Fig. 1), chemically equivalent distances and angles may be directly compared in Tables III, IV and V. Lists of observed and calculated structure factors are available from the author.

Results and Discussion

A number of complexes of Ba^{2+} with crown ethers of various inner diameters have been investigated so far [3, 6, 18–20]; in general, 18-membered annular oligoethers with six hetero atoms fit Ba^{2+} and similar sized cations well [2, 3, 18, 21]. This also holds for

TABLE II. Fractional Coordinates (×10^4) and Anisotropic Temperature Factors (Å^2 × 10^4) of Non-hydrogen Atoms in the Cu^{2+} Complex. The temperature factor exponent takes the form $-2\pi^2(U_{11}h^2a^{*2} + .. + 2U_{12}hka^*b^*)$.

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	1798(2)	2555(2)	3238(1)	312(7)	390(8)	376(8)	15(6)	−42(6)	−181(7)
Cl(1)	291(4)	1041(4)	2439(2)	464(14)	583(15)	735(17)	−109(13)	−76(13)	−295(12)
Cl(2)	1420(4)	2275(4)	4743(2)	401(13)	693(16)	371(13)	132(12)	−2(11)	−204(12)
N(1)	3290(8)	4002(7)	3555(5)	329(23)	411(23)	251(23)	−26(22)	9(21)	−193(21)
C(2)	5140(9)	3262(11)	3822(6)	311(24)	517(25)	295(25)	110(24)	−104(23)	−218(22)
C(3)	6222(8)	4200(9)	4012(7)	280(24)	781(23)	355(22)	85(21)	−93(24)	−310(26)
C(4)	5363(14)	5910(12)	3931(7)	417(23)	404(23)	433(22)	0(21)	17(21)	−231(23)
C(5)	3434(14)	6647(12)	3664(6)	509(23)	382(24)	317(26)	−2(24)	10(23)	−210(24)
C(6)	2447(11)	5627(8)	3473(5)	317(24)	356(24)	163(24)	43(22)	−36(22)	−180(22)
C(7)	308(12)	6454(11)	3234(6)	306(24)	365(25)	368(25)	−124(24)	39(23)	−97(23)
S(8)	−722(3)	5064(3)	2651(2)	251(11)	427(13)	326(12)	14(10)	2(10)	−137(10)
C(9)	−266(12)	5014(10)	1511(6)	319(24)	285(24)	408(25)	−17(24)	62(23)	−103(22)
C(10)	−1437(13)	6512(12)	928(7)	476(25)	521(26)	411(16)	−11(25)	63(24)	−190(24)
O(11)	−1052(10)	7913(9)	1170(5)	656(24)	516(24)	527(24)	−61(22)	114(23)	−270(22)
C(12)	65(15)	8264(13)	617(7)	699(26)	591(26)	494(26)	117(25)	104(25)	−341(24)
C(13)	2133(15)	7441(13)	980(7)	727(26)	673(26)	501(26)	−39(25)	188(25)	−476(24)
O(14)	2826(9)	5758(9)	792(5)	466(23)	620(24)	455(24)	45(22)	−59(22)	−334(24)
C(15)	4720(14)	4816(15)	1276(8)	428(25)	1085(27)	562(27)	92(26)	−9(25)	−473(24)
C(16)	5239(13)	3042(14)	1161(7)	245(25)	939(27)	462(26)	157(26)	16(24)	−82(25)
O(17)	4050(10)	2523(9)	1550(5)	550(24)	567(24)	636(25)	39(23)	261(23)	−69(22)
C(18)	4349(15)	838(13)	1499(8)	560(26)	527(26)	564(26)	−35(26)	86(26)	−59(25)
C(19)	5600(15)	−179(13)	2335(9)	624(26)	509(26)	740(27)	−112(26)	176(26)	−62(25)
S(20)	4761(4)	298(3)	3385(7)	382(13)	289(12)	515(14)	60(11)	−62(11)	−120(10)
C(21)	6103(14)	1424(12)	3989(8)	474(25)	531(26)	617(26)	2(25)	−202(25)	−238(24)

TABLE III. Bond Lengths (Å).

Atoms	Distance (Å)	
	1	*2*
N(1)–C(2)	1.351(9)	1.325(8)
N(1)–C(6)	1.331(8)	1.314(8)
C(2)–C(3)	1.395(14)	1.391(16)
C(6)–C(5)	1.412(14)	1.392(9)
C(3)–C(4)	1.368(13)	1.382(4)
C(5)–C(4)	1.368(12)	1.378(4)
C(6)–C(7)	1.501(10)	1.523(11)
C(2)–C(21)	1.477(10)	1.496(13)
C(7)–S(8)	1.787(8)	1.824(11)
C(21)–S(20)	1.825(10)	1.814(12)
S(8)–C(9)	1.833(10)	1.822(11)
S(20)–C(19)	1.802(8)	1.808(14)
C(9)–C(10)	1.498(13)	1.475(12)
C(19)–C(18)	1.499(12)	1.505(15)
C(10)–O(11)	1.421(10)	1.398(15)
C(18)–O(17)	1.436(12)	1.405(14)
O(11)–C(12)	1.462(11)	1.455(16)
O(17)–C(16)	1.452(11)	1.425(16)
C(12)–C(13)	1.452(14)	1.494(14)
C(16)–C(15)	1.505(15)	1.458(16)
C(13)–O(14)	1.444(11)	1.396(13)
C(15)–O(14)	1.429(9)	1.446(11)
S(22)–C(23)	1.641(7)	–
C(23)–N(24)	1.151(9)	–
S(25)–C(26)	1.623(10)	–
C(26)–N(27)	1.136(13)	–
O(28)–H(1)	0.883(16)	–
O(28)–H(2)	0.922(17)	–

TABLE IV. Bond Angles (°).

Atoms	Angle (°)	
	1	*2*
C(2)–N(1)–C(6)	118.7(7)	120.8(8)
N(1)–C(2)–C(3)	121.5(6)	120.2(2)
N(1)–C(6)–C(5)	122.5(6)	122.2(6)
N(1)–C(2)–C(21)	117.5(8)	121.4(9)
N(1)–C(6)–C(7)	117.7(7)	119.8(9)
C(3)–C(2)–C(21)	121.0(7)	118.3(2)
C(5)–C(6)–C(7)	119.8(6)	117.8(6)
C(3)–C(4)–C(5)	120.4(10)	118.6(3)
C(6)–C(7)–S(8)	111.1(5)	112.0(5)
C(2)–C(21)–S(20)	109.9(6)	113.5(6)
C(7)–S(8)–C(9)	101.1(4)	103.7(5)
C(21)–S(20)–C(19)	101.4(4)	103.3(6)
S(8)–C(9)–C(10)	108.9(6)	115.9(6)
S(20)–C(19)–C(18)	116.4(5)	117.6(7)
C(9)–C(10)–O(11)	109.7(6)	115.2(8)
C(19)–C(18)–O(17)	109.9(6)	113.4(9)
C(10)–O(11)–C(12)	111.7(6)	114.6(8)
C(18)–O(17)–C(16)	111.7(6)	117.3(8)
O(11)–C(12)–C(13)	109.5(6)	113.1(9)
O(17)–C(16)–C(15)	109.1(6)	109.4(9)
C(12)–C(13)–O(14)	108.9(9)	111.2(10)
C(16)–C(15)–O(14)	108.7(8)	111.0(10)
C(13)–O(14)–C(15)	112.2(8)	114.0(9)
S(22)–C(23)–N(24)	179.2(8)	–
S(25)–C(26)–N(27)	178.6(7)	–
H(1)–O(28)–H(2)	95(4)	–

the present ligand (see Fig. 2): the alkaline earth metal ion is kept in the centre of the cavity by interactions with all six hetero atoms of the macrocycle at distances slightly longer than the sum of the respective ionic and van der Waals radii Ba..O = 2.74, Ba..N = 2.84, Ba..S = 3.19 Å [12]. All angles with Ba^{2+} as vertex are 60 ± 2° but the hexagon formed is fairly distorted: diagonals vary from 5.635(10) [N(1)..O(14)] to 6.074(9) Å [S(20)..O(11)], and angles which should be 120° vary from 103.5(6) [N(1)..S(20)..O(17)] to 129.1(5)° [S(8)..N(1).. S(20)]. Moreover, only four hetero atoms O(11), O(14), O(17) and S(20) are coplanar with the cation to within ± 0.03 Å whilst N(1) and S(8) deviate by 1.49(2) and 1.79(2) Å from this plane. Models indicate that these irregularities must mostly be attributed to the diverse radii of coordinating atoms, especially to the large S atoms as compared to O or N, and are not a consequence of the rigid pyridine moiety; torsion angles in the macrocycle involving N as an inner atom meet the requirements C–C–X–C = 180° [22] and thus would allow approximate co-planarity of (similar sized) hetero atoms. Only the X–C–C–X angles constrained to 0° as in benzo-18-crown-6·$Ba(ClO_4)_2$ [18] instead of 60° [22] prevent co-planarity; in the respective dicyclohexyl-18-crown-6 complex (with only sp^3-hybridised C atoms) it can again be achieved [3].

Ba^{2+} is further coordinated to two ^-NCS anions in one apical region and to one water molecule in the opposite one. The two different angles Ba..N(24)–CS = 155.8(7)° and Ba..N(27)–CS = 176.3(6)° probably explain the splitting of the C–N stretching frequencies in the i.r. spectrum of *1* [11], similar to that in a complex of benzo-15-crown-5 with $Ca(SCN)_2$ [23]. The resulting rather asymmetric overall arrangement of ligating atoms appears frequently with Ba^{2+} complexes [3, 18] and indicates predominantly electrostatic interactions.

Though the existence of a stable complex of 18-crown-6 with Cu^{2+} has been reported [8b], 12-membered rings containing four hetero atoms fit this

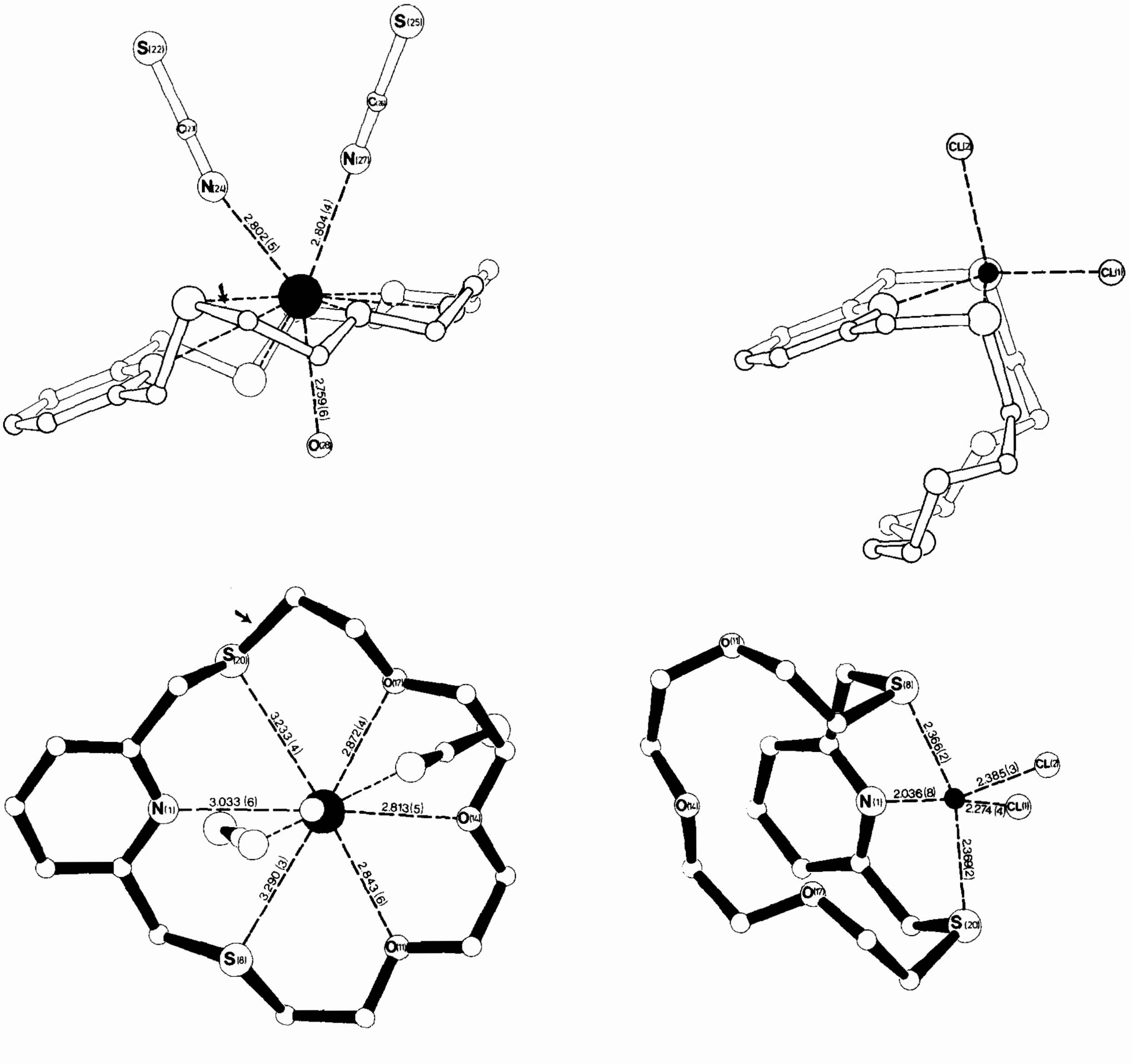


Fig. 2. Perspective views of the Ba^{2+} complex (left) and of the Cu^{2+} complex (right). Radii are arbitrary, H atoms are omitted for the sake of clarity.

small d^9 metal ion much better [24, 25], not only with respect to its diameter but also with respect to its requirements for a square-planar, square-pyramidal or octahedral environment [13]. With the O atoms of the larger 15-crown-5, Cu^{2+} is linked solely through water molecules [26]; only when more than two C atoms between hetero atoms render a macrocycle sufficiently flexible to allow a suitable arrangement is a complex of Cu^{2+} and an annular ligand with five N atoms facilitated [27]. With a very large ring, however, a binuclear complex can be formed [28]. In this, as in a Cu^{2+} complex with the 18-crown-6 analogue 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane ('tdco') [29], nitrogen is preferred as a donor atom and some or all oxygens are 'ignored'.

A similar pattern is displayed in the present structure *2* where N(1), S(8) and S(20) and one chloride (being co-planar to within ±0.04 Å) form the basal plane of a square pyramid, the apex of which is occupied by the second anion (Fig. 2). The ether chain of the ligand is folded away from the metal, preventing any additional coordination of the water

TABLE V. Torsion Angles along the Macrocycle. Mean e.s.d. s are 2°. Considerable deviations from expected values *gauche* (G) or *trans* (T) are indicated by arrows.

Atoms				Torsion Angles (°)		
				1	*2*	
N(1)	C(6)	C(7)	S(8)	53	−24 ←	G
N(1)	C(2)	C(21)	S(20)	55	23 ←	G
C(6)	C(7)	S(8)	C(9)	−160 ←	−75 ←	T
C(2)	C(21)	S(20)	C(19)	−170	92 ←	T
C(7)	S(8)	C(9)	C(10)	158 ←	−74 ←	T
C(21)	S(20)	C(19)	C(18)	73 ←	−104 ←	T
S(8)	C(9)	C(10)	O(11)	−69	71	G
S(20)	C(19)	C(18)	O(17)	56	64	G
C(9)	C(10)	O(11)	C(12)	176	102 ←	T
C(19)	C(18)	O(17)	C(16)	160	95 ←	T
C(10)	O(11)	C(12)	C(13)	173	−90 ←	T
C(18)	O(17)	C(16)	C(15)	180	180	T
O(11)	C(12)	C(13)	O(14)	66	77	G
O(17)	C(16)	C(15)	O(14)	−68	−64	G
C(12)	C(13)	O(14)	C(15)	172	−168	T
C(16)	C(15)	O(14)	C(13)	−178	171	T
C(21)	C(2)	N(1)	C(6)	177	175	T
C(7)	C(6)	N(1)	C(2)	179	−175	T

TABLE VI. Mean Bond Lengths (Å) and Angles (°) in Both Complexes.

	1	2
Mean Distances (Å)		
C–C	1.49(1)	1.49(1)
C–O	1.44(1)	1.42(1)
C–S	1.81(1)	1.82(2)
Mean Angles (°)		
C–O–C	111.9(7)	115.3(8)
O–C–C	109.3(7)	112.2(9)
C–S–C	101.3(7)	103.5(5)

TABLE VII. H Atom Parameters in *1* (top) and *2* (bottom).

Atom	x	y	z	U
H(3)	7423	4032	3470	500
H(4)	8251	4586	6163	500
H(5)	8906	6271	7539	500
H(7a)	9099	7817	7509	500
H(7b)	9948	7627	6055	500
H(9a)	9677	9266	6106	500
H(9b)	8670	10018	7514	500
H(10a)	8285	10937	5913	500
H(10b)	6601	10512	5588	500
H(12a)	7342	11108	3545	500
H(12b)	5802	10495	3045	500
H(13a)	8452	9695	1620	500
H(13b)	6732	10375	950	500
H(15a)	6051	9030	−1196	500
H(15b)	7815	8294	−762	500
H(16a)	5819	7290	−2438	500
H(16b)	4854	7787	−974	500
H(18a)	5403	6052	−599	500
H(18b)	5778	5768	−2348	500
H(19a)	6944	4420	−1349	500
H(19b)	8264	4933	−1640	500
H(21a)	6943	4349	1277	500
H(21b)	6069	5608	1487	500
H(3)	7731	3593	4223	500
H(4)	6186	6654	4074	500
H(5)	2708	7981	3604	500
H(7a)	−220	6830	3851	500
H(7b)	−100	7534	2799	500
H(9a)	−493	3975	1180	500
H(9b)	1187	4828	1572	500
H(10a)	−2890	6812	951	500
H(10b)	−1228	6226	244	500
H(12a)	−239	7837	−57	500
H(12b)	−329	9588	585	500
H(13a)	2403	7570	1705	500
H(13b)	2842	8035	672	500
H(15a)	5683	5186	1019	500
H(15b)	4807	5068	1988	500
H(16a)	6685	2374	1494	500
H(16b)	5079	2790	448	500
H(18a)	3004	743	1402	500
H(18b)	4993	339	925	500
H(19a)	5844	−1460	2203	500
H(19b)	6915	−29	2436	500
H(21a)	7436	998	3777	500
H(21b)	6342	1159	4706	500

present in the copper salt used for the preparation [11]. The cation is located 0.382(8) Å above the base, and coordination angles (ideal value 90°) vary from 84.4(7) [S(8)..Cu..N(1)] to 104.5(6) [S(8)..Cu..Cl(2)], average 94°. Though slightly distorted geometry is a common feature with Cu^{2+} complexes, some of the disparities are probably again due to the different radii of ligating atoms.

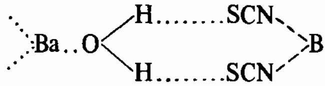
All cation..dipole and cation..anion interactions must be considered strong since distances are about 0.2 Å shorter than the sum of the respective van der Waals and ionic radii [12]; they are comparable to those in copper complexes with a fitting tetrathiaether [25] or N-containing macrocycles [27, 28] but appreciably shorter than in the complex with 'tdco' [29] where four out of the six hetero atoms are coordinated. The differences in distances $Cu^{2+}..Cl(1)^-$ = 2.274(4) and $Cu^{2+}..Cl(2)^-$ = 2.385(3) Å confirm former results [24, 27–29], namely that equatorial bonds in general are stronger than apical ones.

The diverse types of wrapping of the cations are reflected in the sequence of torsion angles in both conformations of the ligand. In analogy to crown ethers [22], strain-free values are 180° (*trans*), usually observed for C–X–C–C, and ±60° (*gauche*), usually encountered with X–C–C–X (X = O, N, S). It can be seen from Table V that the structure of *1* is relatively strain-free; the torsion angles differ from ideality by only 8° (average) with a maximum deviation of about 20° at the bulky S atoms. The unusual rotation of C(21)–S(20)–C(19)–C(18) to *gauche* is presumably due to steric repulsion (see above).

Examination of the torsion angles in the copper complex, however, reveals the considerably larger disparity between experimental and theoretical values associated with the coordination of a 'non-fitting' cation. The two S atoms are probably brought into positions suitable for coordination to Cu^{2+} (at a distance *ca.* 1 Å shorter than in the respective Ba compound) by narrow angles N(1)–C(6)–C(7)–S(8) and N(1)–C(2)–C(21)–S(20) of *ca.* ± 25°; angles C(6)–C(7)–S(8)–C(9) = –75(2) and C(2)–C(21)–S(20)–C(19) = 92(2)° mark the folding of the ligand. On the other hand, uncommon torsion angles of about 90 to 100° could also reflect conformational disorder of the non-coordinating chain as observed in an uncomplexed cyclic ether before [30]; however, only C(15) and C(16) [and C(5)] display abnormally high anisotropic movement.

In both complexes, the C–C bond lengths of the ligand appear shortened, as is normally observed with crown ethers [31]; widened bond angles in *2* (Table VI) may also provide some evidence for the strained conformation in the copper complex.

The lattice of the Ba^{2+} complex is further stabilised via H bonds S(25)..H(1)^{i} = 2.42(2) and S(22)..H(2)^{i} = 2.46(2) Å (i = 1 + x, y, z) thus linking the complex molecules and giving rise to infinite



chains approximately along x, while there are no additional contacts between complexes in the copper compound.

Acknowledgements

The author is grateful to Prof. F. Vögtle and Dr. E. Weber, Bonn, for providing the samples, and to Prof. W. Saenger, Göttingen, for valuable discussions and kind help with technical problems.

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