of both stretching vibrations, which is not the case in the matrix data. If the Tl^+ covalently interacts instead with a sulfite oxygen, the S–O bond would be weakened, lowering the vibrational frequencies. Electrostatically, the Tl–O interaction would be more likely and is apparently what occurs in crystalline Tl_2SO_3, judging from the relatively low vibrational frequencies.

David and Ault[6] also propose the symmetrical structure, $^-O_2SOSO_2^-$, for the disulfite ions in their matrices. The vibrational frequencies that they assign to this structure are listed in Table I. What is most surprising about this report is the unexpected stability of this oxygen-bridged species, which apparently exceeds that of sulfite. The structure[11] and vibrational spectrum of the disulfite ion in crystalline solids[3,12] and solution[4a,12] is well established. Our room-temperature spectrum of $Tl_2S_2O_5$ closely matches the spectra of the other disulfites (Table I). The disulfite spectrum is also known in low-temperature matrices.[13] Normally, disulfite has an unsymmetrical structure, which can be described as a sulfonate group and a sulfinate group connected by a somewhat long[11] sulfur–sulfur bond. There is no evidence in solution[4] or otherwise for the symmetrical structure with an oxygen atom bridging two SO_2^- groups. A substantial part of the argument for the symmetric disulfite structure in the matrices[6] rests on the assignment to a bridging oxygen stretching mode an infrared band at 776 cm^{-1}. However, the dithionate ion ($S_2O_6^{2-}$) also has a band in this region,[14] but has no bridging oxygen, and Connick and co-workers have convincingly shown that a Raman band with a similar frequency in the bisulfite–disulfite aqueous solution spectrum[4a] belongs to an S–(OH) stretching vibration of the SO_3H^- isomer of bisulfite.[4b] There is theoretical support for this latter assignment.[10] Finally, in the low-temperature matrix experiments,[6] only three of the eleven infrared bands, which were assigned the symmetric disulfite, shifted when oxygen-18 was used in place of normal oxygen. Theoretically, all of the bands should have shifted measurably, which is our ^{18}O experience with the unsymmetric disulfite,[3] with the bands in the S–O stretching region shifting in the 30–50-cm^{-1} range. This indicates that secondary reaction products are probably being formed. Both thallium and sulfur can occur in more than one common oxidation state. Either the hot molecular beams of Tl_2O monomers and dimers, which converge with the SO_2 just before deposition, or traces of water or hydroxide, which are notoriously difficult to totally eliminate in matrix work with metal oxides, are fully capable of initiating the complex autoredox reactions, which oxysulfur compounds of intermediate oxidation state are known to undergo.[15] The infrared spectra of the matrix reaction products are not inconsistent with the existence of polythionates, polysulfides, and/or other oxysulfur species.

In conclusion, the primary reaction product of the room-temperature reaction of wet, solid TlOH and excess liquid SO_2 is thallium(I) disulfite. It readily decomposes to Tl_2SO_3 and SO_2, and its Raman spectrum indicates that the disulfite ion has the common unsymmetric structure. In contrast, the complex infrared spectra of the reaction products of converging molecular beams of hot Tl_2O vapor and SO_2, trapped in argon matrices at cryogenic temperatures, are not consistent with simple $Tl_2S_2O_5$ and Tl_2SO_3 formation but may suggest the formation of polythionates and/or complex mixtures of other oxysulfur species.

---

(11) (a) Lindqvist, I.; Mortsell, M. *Acta Crystallogr.* **1957**, *10*, 406. (b) Baggio, S. *Acta Crsytallogr., Struct. Crystallogr. Cryst. Chem.* **1971**, *B27*, 517.

(12) Herlinger, A. W.; Long, T. V. *Inorg. Chem.* **1969**, *8*, 2661.

(13) Meyer, B.; Mulliken, B.; Weeks, H. *Phosphorus Sulfur* **1980**, *8*, 291.

(14) Palmer, W. G. *J. Chem. Soc.* **1961**, 1552.

(15) (a) Meyer, B.; Peter, L.; Ospina, M. *Geochim. Cosmochim. Acta* **1979**, *43*, 1579. (b) Meyer, B.; Ospina, M. *Phosphorus Sulfur* **1982**, *14*, 23.

Notes

Contribution from the Department of Chemistry,
University of the Witwatersrand,
Johannesburg, South Africa

Structures of Bis(1-thia-4,7-diazacyclononane)copper(II) Nitrate and Bis(1,7-diaza-4-thiaheptane)copper(II) Nitrate. A Different Conformation for the Coordinated Macrocycle

Jan C. A. Boeyens,* Susan M. Dobson,[1a]
and Robert D. Hancock*

Received May 15, 1984

Recently we reported the crystal structures of the bis complexes of daes[1b] and (9-ane-N_2S)[2] with nickel(II), but because the bis(1,7-diaza-4-thiaheptane) complex has the sulfur atoms cis to each other, while in the macrocyclic complex they are trans, the complexes were not exactly comparable. Crystal structures of transition-metal complexes $[M(daes)_2]^{n+}$ have been determined for M = Ni(II)[1] and Co(III).[3] In both structures the unsymmetrical facial geometric isomer is found to occur.

Examination of the literature shows that when bonds to copper(II) are distorted, first-row donor atoms will occupy the equatorial positions in preference to second- or third-row donors, which will occupy the axial sites (pseudo-Jahn–Teller distortion). Thus, the tendency of the two sulfurs to occupy the axial sites should lead to the *s-fac* rather than the *u-fac* structure. This would then allow for a direct comparison between the bis(1,7-diaza-4-thiaheptane) copper complex and the bis(1-thia-4,7-diazacyclononane)copper complex. The role of compression[4] around the metal center or distortions[5] of any nature in contributing to the high ligand field strength could therefore be evaluated.

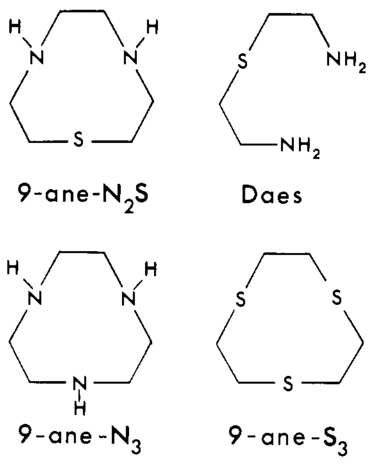

Figure 1. Ligands discussed in this paper.

We report here an improved synthesis of the ligand 9-ane-N_2S (see Figure 1), the electronic spectra of the bis(1-thia-4,7-dia-

---

(1) (a) Formerly Susan M. Hart. (b) Hart, S. M.; Boeyens, J. C. A.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 982–986.

(2) Hart, S. M.; Boeyens, J. C. A.; Michael, J. P.; Hancock, R. D. *J. Chem. Soc., Dalton Trans.* **1983**, 1601–1606.

(3) Hammershøi, A.; Larsen, E.; Larsen, S. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 501–507.

(4) Busch, D. H.; Farmery, K.; Goedken, V.; Katovic, V.; Melnyk, A. C.; Sperati, C. R.; Tokel, N. *Adv. Chem. Ser.* **1971**, *No. 100*, 44.

(5) Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1978**, *28*, L157–L159.

0020-1669/85/1324-3073$01.50/0 © 1985 American Chemical Society

Table I. Crystal Data for the Copper Complexes[a]

	$Cu(9\text{-ane-}N_2S)_2(NO_3)_2$	$Cu(daes)_2(NO_3)_2$
formula	$C_{12}H_{28}N_4S_2CuN_2O_6$	$C_8H_{24}N_4S_2CuN_2O_6$
M_r	480.07	427.99
space group	*Pbca*	$P\bar{1}$
a, Å	14.50 (1)	10.50 (1)
b, Å	10.34 (1)	9.96 (1)
c, Å	12.95 (1)	8.55 (1)
α, deg		90.34 (5)
β, deg		99.67 (5)
γ, deg		89.24 (5)
V, Å^3	1942.05	882.38
Z	4	2
d_{obsd},[b] g cm^{-3}	1.64 (1)	1.62 (1)
d_{calcd}, g cm^{-3}	1.64	1.61
cryst color	purple	dark blue
radiation, Å	$\lambda(MoK\alpha)$ 0.7107	$\lambda(MoK\alpha)$ 0.7107
data collecn	ω scan	$\omega/2\theta$ scan
θ limits, deg	$3 \leqslant \theta \leqslant 23$	$3 \leqslant \theta \leqslant 23$
scan speed, deg s^{-1}	0.056	0.043
scan width, deg	1.4	1.3
bkgd count time, s	25.04	30.02
no. of unique data	1347	2399
no. of data used	1315	2399
abs coeff (μ_λ), cm^{-1}	13.09	14.35
final R	0.034	0.043

[a] The standard deviation of the least significant figure is given in parentheses. [b] The densities were determined by the flotation method in a solution of carbon tetrachloride and 1,2-dibromoethane.

zacyclononane) and bis(1,7-diaza-4-thiaheptane)copper(II) complexes, and the crystal structures of the complexes $[Cu(9\text{-ane-}N_2S)_2](NO_3)_2$ and $[Cu(daes)_2](NO_3)_2$.

Experimental Section

The yield in the condensation step of the synthesis of cyclic triamines can be increased significantly if the ditosylate of 1,2-ethanediol is used instead of 1,2-dibromoethane.[6] Similarly we were able to improve the yield in the synthesis of the ditosylate of 1-thia-4,7-diazacyclononane from 10% to 49%.

4,7-Bis((4-methylphenyl)sulfonyl)-1-thia-4,7-diazacyclononane. *N,N'*-Bis((4-methylphenyl)sulfonyl)bis(2-aminoethyl) sulfide (59.287 g, 0.138 mol) was added to 500 mL of absolute ethanol in which sodium metal (8.507 g, 0.370 mol) had been dissolved. The solution was stirred for 20 h before a fine white precipitate (61.6 g, 0.129 mol, 93% yield) was filtered off and washed with diethyl ether. The sodium salt of the ditosylate (51.1 g, 0.108 mol) was then dissolved in 1 L of DMF and heated to 110 °C. A solution of 1,2-bis((4-methylphenyl)sulfonyl)ethane[7] (41.2 g, 0.111 mol) in 400 mL of DMF was added dropwise over 3 h to this heated solution and then stirred for a further 20 h. The solution was evaporated down to a honey-colored solid, 500 mL of water was added to the solid, and the mixture was then extracted into hot toluene. The toluene extract was dried over $MgSO_4$ and concentrated to 5% of its original volume, and a fine cream precipitate (24.0 g, 0.053 mol; 48.8% yield) was filtered off; mp 276–279 °C. This agrees with the value we reported earlier.[2] Hydrolysis of this product[2] resulted in the dihydrobromide salt.

Preparation of $[Cu(9\text{-ane-}N_2S)_2](NO_3)_2$. A slight excess of $(9\text{-ane-}N_2S)\cdot 2HBr$ was neutralized with sodium ethoxide in ethanol. The sodium bromide was filtered off, and the solution was then added to $Cu(NO_3)_2\cdot 3H_2O$ dissolved in a minimum amount of ethanol. On cooling, purple crystals were obtained, which were washed with ethanol followed by ether.

IR (KBr): 3090, 2920, 2880, 1460, 1390–1350 (s, NO_3^-), 1220, 1095, 1080, 992, 788 cm^{-1}. UV/vis λ_{max} (ϵ):556 (53), 270 nm (5849). Anal. Calcd for $CuC_{12}H_{28}N_6O_6S_2$: C, 30.02; H, 5.88; N, 17.51. Found: C, 30.00; H, 6.09; N, 17.42.

Preparation of $[Cu(daes)_2](NO_3)_2$. A 0.170-g sample of daes (K and K Chemicals) in methanol was added to 0.164 g of $Cu(NO_3)_2\cdot 3H_2O$ in methanol and the mixture allowed to stand. Thin purple flakes were obtained that were not suitable for X-ray diffraction techniques. Suitable single crystals were obtained by recrystallization from a water/dimethylformamide mixture. IR (KBr): 3210, 3115, 2930, 2870, 1590, 1570, 1400–1350 (s, NO_3^-), 1140, 1060, 830 cm^{-1}. UV/vis λ_{max} (ϵ): 615 (68), 323 nm (1252). Anal. Calcd for $CuC_8H_{24}N_6O_6S_2$: C, 22.45; H, 5.65; N, 19.64. Found: C, 22.41; H, 5.62; N, 19.29.

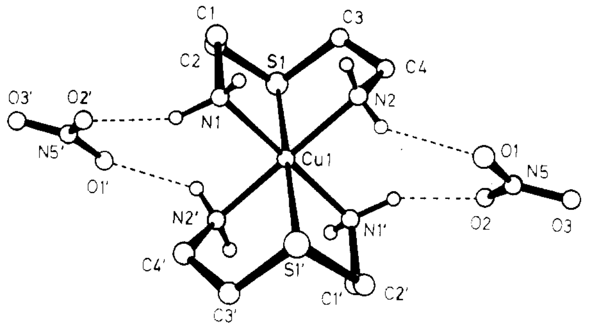

Figure 2. ORTEP[9] diagram of one $[Cu(daes)_2](NO_3)_2$ molecule showing the numbering scheme. The other molecule has a similar numbering scheme, with N(3) in place of N(1), C(5) in place of C(1), etc. Hydrogen bonding is indicated by the dashed lines.

Table II. Fractional Atomic Coordinates for $[Cu(9\text{-ane-}N_2S)_2](NO_3)_2$[a]

atom	x	y	z
Cu	0.0000	0.5000	0.5000
S	−0.0846 (1)	0.2978 (1)	0.4070 (1)
N(1)	−0.0226 (2)	0.3983 (3)	0.6314 (2)
N(2)	−0.1364 (2)	0.5540 (3)	0.5169 (2)
C(1)	−0.0976 (3)	0.2153 (4)	0.5312 (3)
C(2)	−0.0304 (3)	0.2573 (4)	0.6151 (3)
C(3)	−0.1007 (3)	0.4613 (4)	0.6861 (3)
C(4)	−0.1755 (3)	0.4947 (4)	0.6114 (3)
C(5)	−0.1930 (3)	0.5268 (4)	0.4238 (3)
C(6)	−0.1929 (3)	0.3843 (4)	0.3928 (3)
N(3)	−0.1193 (2)	0.6390 (3)	0.1480 (2)
O(1)	−0.0883 (2)	0.5370 (3)	0.1827 (2)
O(2)	−0.1487 (3)	0.7200 (3)	0.2079 (3)
O(3)	−0.1239 (2)	0.6571 (3)	0.0538 (2)

[a] Non-hydrogen atoms.

Table III. Important Bond Lengths and Angles in the $Cu(9\text{-ane-}N_2S)_2$ Cation

	Length (Å)		
Cu–S	2.707 (1)	S–C(1)	1.830 (4)
Cu–N(1)	2.027 (3)	S–C(6)	1.817 (4)
Cu–N(2)	2.067 (3)		
	Angle (deg)		
N(1)–Cu–S	84.2 (1)	N(1)–Cu–N(2)'	95.9 (1)
N(2)–Cu–S	79.8 (1)	C(1)–S–Cu	90.9 (1)
N(1)–Cu–N(2)	84.1 (1)	C(6)–S–Cu	93.2 (1)
N(1)–Cu–S'	95.8 (1)	C(1)–S–C(6)	103.2 (2)
N(2)–Cu–S'	100.2 (1)		

Spectroscopic Measurements. UV/visible spectra were recorded on a Cary 219 spectrophotometer, NMR spectra on a Varian EM360, and IR spectra as KBr pellets on a Perkin-Elmer 580B infrared spectrophotometer.

Intensity data and accurate cell dimensions were obtained at room temperature with a Philips PW 1100 diffractometer using Mo Kα radiation (λ = 0.7107 Å; incident beam graphite crystal monochromator). Crystal data for the two complexes are given in Table I. The structures were determined by using Patterson and Fourier techniques with the SHELX[8] program.

Results and Discussion

The bis open-chain complex $[Cu(daes)_2](NO_3)_2$ (Figure 2) contains a copper atom facially coordinated to two daes molecules such that the sulfur atoms are trans. This is therefore the first example of a symmetrical facial coordination of daes to a transition metal—the crystal structures of the bis(1,7-diaza-4-thiaheptane) complexes of nickel(II)[1] and cobalt(III)[3] and the circular dichroism

---

(6) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268–2270.

(7) Sakellarios, E. J. *Helv. Chim. Acta* **1946**, *29*, 1675–1684.

(8) Sheldrick, G. M. In "Computing in Crystallography"; Schenk, H., Olthof-Hazelkamp, R., Eds.; Delft University Press: Delft, Holland, 1978.

(9) Johnson, C. K. "ORTEP", Report ORNL-3794, Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Table IV. Fractional Atomic Coordinates for $[Cu(daes)_2](NO_3)_2$[a]

atom	x	y	z
	Molecule 1		
Cu(1)	0.0	0.0	0.0
S(1)	0.2498 (1)	−0.0587 (1)	0.1371 (1)
N(1)	0.0909 (4)	0.0747 (4)	−0.1773 (5)
N(2)	0.0149 (4)	−0.1918 (4)	−0.0825 (5)
C(1)	0.2204 (4)	0.0179 (5)	−0.1838 (6)
C(2)	0.3073 (5)	0.0273 (5)	−0.0255 (7)
C(3)	0.2396 (5)	−0.2303 (5)	0.0627 (6)
C(4)	0.1037 (5)	−0.2826 (5)	0.0215 (6)
N(5)	−0.2673 (4)	−0.3924 (4)	0.0417 (4)
O(1)	−0.2163 (3)	−0.3518 (4)	−0.0713 (4)
O(2)	−0.3577 (4)	−0.4709 (4)	0.0118 (5)
O(3)	−0.2250 (6)	−0.3520 (4)	0.1757 (4)
	Molecule 2		
Cu(2)	0.5	0.5	0.5
S(2)	0.4388 (1)	0.2412 (1)	0.5756 (1)
N(3)	0.5680 (4)	0.4032 (4)	0.3175 (5)
N(4)	0.3126 (4)	0.4923 (4)	0.3809 (5)
C(5)	0.5156 (5)	0.2675 (5)	0.2770 (6)
C(6)	0.5251 (5)	0.1769 (5)	0.4220 (7)
C(7)	0.2762 (5)	0.2584 (5)	0.4636 (6)
C(8)	0.2251 (5)	0.4012 (5)	0.4493 (6)
N(6)	0.1106 (4)	0.7638 (4)	0.5275 (4)
O(4)	0.1506 (4)	0.7457 (4)	0.4011 (4)
O(5)	0.1598 (3)	0.6978 (4)	0.6474 (4)
O(6)	0.0230 (3)	0.8465 (4)	0.5374 (4)

[a] Non-hydrogen atoms.

Table V. Important Bond Lengths (Å) and Angles (deg) in the $Cu(daes)_2$ Cations

bond	molecule 1	molecule 2
Cu(1)–S(1)	2.745 (1)	2.772 (1)
Cu(1)–N(1)	2.070 (4)	2.053 (4)
Cu(1)–N(2)	2.046 (4)	2.061 (4)
C(2)–S(1)	1.828 (6)	1.826 (6)
C(3)–S(1)	1.819 (5)	1.819 (5)

angle	molecule 1	molecule 2
N(1)–Cu(1)–S(1)	82.1 (1)	82.6 (1)
N(2)–Cu(1)–S(1)	80.5 (1)	80.3 (1)
N(1)–Cu(1)–N(2)	91.2 (2)	91.6 (2)
N(1)–Cu(1)–S(1)′	97.9 (1)	97.4 (1)
N(2)–Cu(1)–S(1)′	99.5 (1)	99.7 (1)
N(1)–Cu(1)–N(2)′	88.8 (2)	88.4 (2)
C(2)–S(1)–Cu(1)	89.6 (2)	89.3 (2)
C(3)–S(1)–Cu(1)	92.6 (5)	91.8 (2)
C(2)–S(1)–C(3)	100.9 (3)	100.7 (2)

studies of the rhodium(III)[10] complex have shown that daes has an unsymmetric facial coordination in all three cases.

The two molecules in the unit cell are similar in all respects. Table V shows that the bond lengths and angles are those expected in coordination compounds. This includes the elongated Cu–S bond, which falls in the range 2.56–2.82 Å as expected for axial Cu–S bonds.[11] The conformations of the four chelate rings in the previously reported bis(1,7-diaza-4-thiaheptane) complexes are all the same for a given complex, ie. $\Delta(\delta\delta)(\delta\delta)$ and $\Delta(\lambda\lambda)(\lambda\lambda)$ for Ni(II)[1] and Co(III),[3] respectively, whereas in the copper complex the conformation is $(\delta\delta)(\lambda\lambda)$. The degree of puckering of the five-membered rings[12] in both the nickel and copper daes complexes is the same (see Table VI).

The bis macrocyclic complex $[Cu(9\text{-ane-}N_2S)_2](NO_3)_2$ contains a Cu(II) ion facially coordinated to two 9-ane-N_2S ligands (see Figure 3). The same environment is found around the nickel ion in the analogous $[Ni(9\text{-ane-}N_2S)_2]^{2+}$ complex except that in the latter there is no elongation of the trans Ni–S bonds.[2] If the two copper complexes (Tables III and V) are compared, it is seen that the metal–donor bonds are similar and that the Cu–S is still elongated. However Glass et al.[13] found in the copper complex of the ligand 9-ane-S_3 that all three Cu–S bonds were similar, 2.43 Å, and postulated that the rigidity of the ligand prevented Jahn–Teller distortion of the hexasulfur octahedron. X-ray diffraction is a time-averaging technique, and two short Cu–S bonds of 2.3 Å and one long bond of 2.7 Å[14] would average out to 2.43 Å. This, together with our results, suggest that these tridentate cyclic ligands are not sufficiently rigid to prevent distortions.

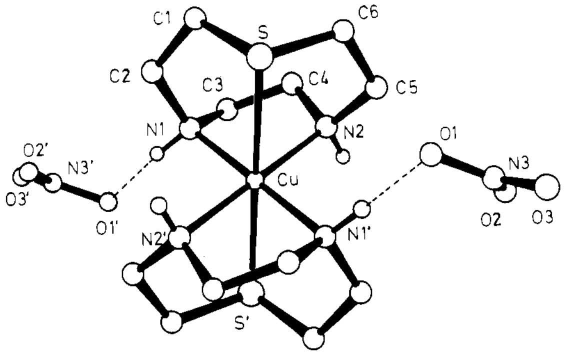

Figure 3. ORTEP[9] diagram of $[Cu(9\text{-ane-}N_2S)_2](NO_3)_2$ showing the numbering scheme. Hydrogen bonding is indicated by the dashed lines.

Table VI. Puckering Parameters for 5-Membered Rings in Bis Macrocyclic and Open-Chain Complexes of Ni(II) and Cu(II)[a]

ring	Q	ϕ	conformn	
	$Ni(9\text{-ane-}N_2S)_2{}^{2+}$			
Ni–S–C–C–N(1)	0.489	57	λ	${}^3_2T$
Ni–N(1)–C–C–N(2)	0.494	45	λ	2^E–${}^3_2T$
Ni–N(2)–C–C–S	0.450	67	λ	${}^3_2T$–${}^3E$
	$Cu(9\text{-ane-}N_2S)_2{}^{2+}$			
Cu–S–C–C–N(1)	0.410	293	δ	${}^4E$
Cu–N(1)–C–C–N(2)	0.402	64	λ	${}^3_2T$–${}^3E$
Cu–N(2)–C–C–S	0.516	34	λ	2^E
	$Ni(daes)_2{}^{2+}$			
Ni–N(1)–C–C–S(1)	0.453	265	δ	${}^4_3T$
Ni–S(1)–C–C–N(2)	0.481	293	δ	${}^4E$
Ni–N(3)–C–C–S(2)	0.422	233	δ	${}^2_3T$
Ni–S(2)–C–C–N(4)	0.458	284	δ	${}^4E$
	$Cu(daes)_2{}^{2+}$[b]			
Cu–N(1)–C–C–S(1)	0.464 (0.467)	260 (266)	δ	3^E–${}^4_3T$
Cu–S(1)–C–C–N(2)	0.442 (0.461)	298 (291)	δ	${}^4E$–${}^4_5T$

[a] For the second ligand bound to the metal, Q remains the same, $\phi = \phi \pm 180°$, λ becomes δ and ${}^2_3T$ becomes ${}^3_2T$ etc. [b] Values for molecule 2 are given in parentheses.

There is a large difference between the values for the two S–Cu–N angles, being 84.2 and 79.8°; one is about 2° larger than the average in the open-chain complex and the other about 2° smaller. This is a result of the nonsymmetric conformation of the macrocyclic ring as described below. The N–Cu–N angle of 84.1° is similar to the undistorted chelate ring found in the complex $[Cu(en)_3]^{2+}$ (82.6°).[15]

The conformation of the 5-membered rings is $(\delta\lambda\lambda)(\lambda\delta\delta)$ (see Table VI) for the complex. However it is the two rings containing both nitrogen and sulfur that have different conformations. This is not the case in the nickel macrocyclic complex where the three 5-membered rings all have the same conformation, i.e. Ni$(\lambda\lambda\lambda)(\delta\delta\delta)$. The degree of puckering, Q, varies much more over

---

(10) Galsbøl, F.; Hammershøi, A.; Larsen, E. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 643–646.
(11) Cambridge Data Centre Files, 1983 update.
(12) For a definition of the parameters $Q + \phi$, see: Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354–1358.
(13) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266–271.
(14) Drew, M. G. B.; Rice, D. A.; Richards, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2503–2508.
(15) Bertini, I.; Dapporto, P.; Gatteschi, D.; Scozzafava, A. *J. Chem. Soc., Dalton Trans.* **1979**, 1409–1414.

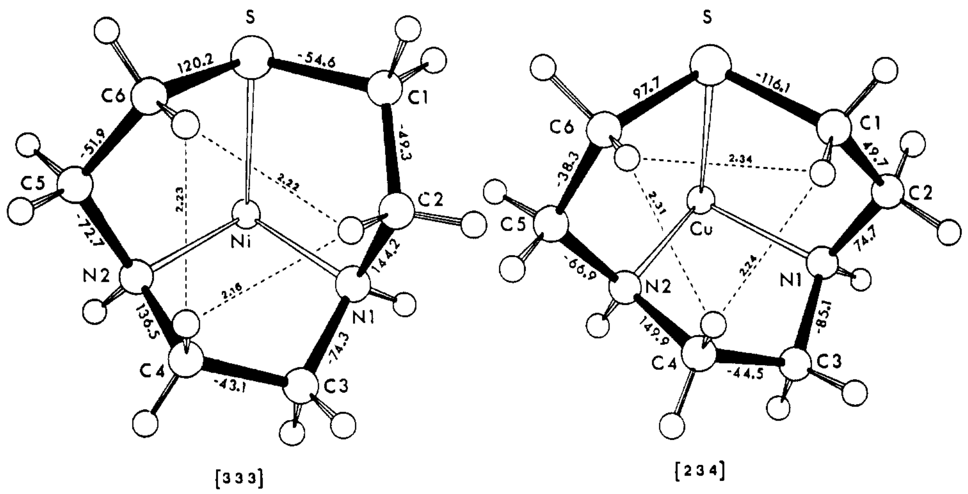

Figure 4. The two different conformations for a coordinated tridentate cyclononane ring: (a) the [333] conformation for the nickel(II) complex and (b) the [234] conformation for the copper(II) complex.

the three rings in the copper complex than in the nickel complex (Table VI).

Conformation of the 9-Membered ring. This flip of conformation of one chelate ring relative to the other two is also manifested in the conformation of the 9-membered ring, as might be expected. The macrocycle has a [234] conformation[16] in the copper complex (Figure 4), and this is the first X-ray diffraction study of a complex containing a tridentate 9-membered ring with this conformation. Previously, Dale et al.,[17] using IR techniques, proposed that the free ligand 9-ane-O_3 has this conformation. Crystal structures of $[Ni(9\text{-ane-}N_3)_2]^{2+}$ and $[Ni(9\text{-ane-}N_2S)_2]^{2+}$ and of 9-ane-S_3 as a free ligand[18] and coordinated to nickel, cobalt, and copper[13] all have a [333] conformation in the 9-membered ring.

The free ligand 9-ane-S_3 has a 3-fold axis perpendicular to the ring and as such has a conformation that most resembles the minimum energy [333] conformation calculated for cyclononane.[18] When two macrocycles are bonded to a metal ion, there is an increase in the number and/or magnitude of nonbonded interactions, either interligand or intraligand. Figure 4 shows that in the [333] conformation, there are three hydrogen atoms "above" the ligand, which are fairly close together (2.16, 2.22, and 2.23 Å), but in the [234] conformation these nonbonded interactions are reduced since these three distances are increased (2.24, 2.31, and 2.34 Å).

We propose that the larger Cu-S bond distance allows this change in conformation from [333] to [234] to take place and that this in turn reduces unfavorable nonbonded interactions and therefore the strain energy of the complex.

In Figure 4 it is also possible to see another result of this conformation change. If the hydrogens on the carbon atoms of the N-C-C-N linkage are to be staggered, then one N-Cu-S angle must be compressed and the Cu-N bond is stretched while the N-Cu-S angle in the other ring must be opened out and the bond compressed.

Electronic Spectra. The spectrum of the macrocyclic complex contains bands at higher wavenumbers (17 990 and 37 040 cm^{-1}) than the spectrum of the open-chain complex (16 260 and 30 960 cm^{-1}, respectively). The increase in ligand field strength indicated by the bands in the 17 000-cm^{-1} region of the spectrum is a phenomenon commonly observed in macrocyclic complexes. Two theories exist for cyclononane ligands: (1) trigonal distortion around the metal[5] and (2) an increase in the number of secondary nitrogens without an increase in steric hindrance.[19] In these two structures the coordination sphere around the metal is the same. The bond lengths to the donor atoms and the bond angles around the metal are similar. The average Cu-N bond lengths are 2.05 and 2.06 Å, and the average N-Cu-S bond angles are 82.0 and 81.4° for the macrocyclic and open-chain complexes, respectively. The differences are within the limits of experimental error. As mentioned earlier the Cu-S bond length is shortened by 0.05 Å in the macrocyclic complex (a similar shortening is found in the nickel complex). It seems likely that the constraints imposed by the macrocyclic ligand are responsible for the bond shortening. However, this does not seem a sufficient effect to account for a large different in 10*Dq* between the macrocyclic and open-chain complex. This is particularly so in relation to the bond angles around copper, which were very similar for the macrocyclic and open-chain complexes.

Acknowledgment. Generous financial support from the Council for Scientific and Industrial Research and the Senate Research Grant Committee of the University of the Witwatersrand is acknowledged. J. Albain is thanked for carrying out the X-ray data collection.

Registry No. 9-ane-N_2S, 88194-17-6; $[Cu(9\text{-ane-}N_2S)_2](NO_3)_2$, 96760-86-0; $[Cu(daes)_2](NO_3)_2$, 96760-88-2; *N*,*N'*-bis((4-methylphenyl)sulfonyl)bis(2-aminoethyl) sulfide, 85775-49-1; 1,2-bis((4-methylphenyl)sulfonyl)ethane, 22952-14-3.

Supplementary Material Available: Listings of calculated and observed structure factors, temperature factors, coordinates for hydrogen atoms, and bond lengths and angles for the two complexes (23 pages). Ordering information is given on any current masthead page.

---

(16) Dale, J. *Acta Chem. Scand.* **1973**, *27*, 1115-1129.
(17) Borgen, G.; Dale, J.; Anet, F. A. L.; Krane, J. *J. Chem. Soc., Chem. Commun.* **1974**, 243-245.
(18) Glass, R. S.; Wilson, G. S.; Setzer, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 5068-5069.
(19) Hancock, R. D.; McDougall, G. J. *J. Am. Chem. Soc.* **1980**, *102*, 6551-6553.

Contribution from the Departments of Chemistry,
University of Natal, Durban, South Africa,
and University of the Witwatersrand,
Johannesburg, South Africa

Stability of Ammonia Complexes That Are Unstable to Hydrolysis in Water

Faizel Mulla,[†] Fabrizio Marsicano,*[†] Bandile S. Nakani,[‡]
and Robert D. Hancock*[‡]

Received August 29, 1984

An interesting feature of aqueous phase coordination chemistry is that most metal ions do not form complexes with ammonia. One

---

[†] University of Natal.
[‡] University of the Witwatersrand.

0020-1669/85/1324-3076$01.50/0 © 1985 American Chemical Society