

Crystallography (1974). Enraf–Nonius (1981) *SDP* programs.

Discussion. Table 1* contains final atomic positional parameters for the non-H atoms. Selected distances and angles are listed in Table 2. The structure is illustrated in Fig. 1. H atoms are omitted to simplify the drawing. The structure analysis shows that the title compound is not isostructural with the corresponding chloride derivative $[\text{U}(\text{C}_5\text{H}_5)_3]\text{Cl}$ (Wong *et al.*, 1965), although the pseudo-tetrahedral coordination geometry about the U atom is identical in the two compounds. In the $[\text{U}(\text{C}_5\text{H}_5)_3]\text{Br}$ structure there are two crystallographically independent molecules in the asymmetric unit of the cell. These are geometrically equivalent as shown by comparison of bond distances and angles (Table 2).

The average U–C bond lengths are 2.72 (1) and 2.71 (1) Å, respectively, for the two crystallographically independent molecules, in agreement with the

* Lists of structures amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51640 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

value of 2.74 Å observed in $[\text{U}(\text{C}_5\text{H}_5)_3]\text{Cl}$ (Wong *et al.*, 1965). The angles subtended at the U atom (Table 2) also compare favourably with the corresponding angles in the chlorine compound. The U–Br bond length is significantly longer than that observed in $[\text{U}(\text{C}_5\text{H}_5)_3]\text{Br}$ (Spirlet *et al.*, 1987). This lengthening may result from steric hindrance on the coordination sphere of the uranium. Indeed, there are several short intramolecular Br...C distances (Table 2) in the two independent molecules. Such short contacts have not been observed in the indenide derivative.

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The Solution and Solid-State Structure of a Macrocyclic Silver(I) Complex with 6,9,12-Trioxa-3,15-dithia-21-azabicyclo[15.3.1]hencosa-1(21),17,19-triene

BY GEORGE FERGUSON

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Canada N1G 2W1

AND ANDREW CRAIG, DAVID PARKER AND KAREN E. MATTHES

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England

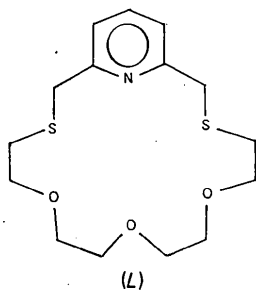
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Abstract. $\text{C}_{30}\text{H}_{46}\text{Ag}_2\text{N}_2\text{O}_6\text{S}_4^{2+} \cdot 2\text{PF}_6^-$, $M_r = 1164.6$, monoclinic, $P2_1/n$, $a = 23.678$ (3), $b = 18.721$ (4), $c = 9.690$ (3) Å, $\beta = 96.31$ (1)°, $V = 4269$ (2) Å³, $Z = 4$, $D_x = 1.81$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 12.7$ cm⁻¹, $F(000) = 2336$, $T = 294$ K, $R = 0.045$ for 3688 observed reflections. In the solid state the cation is dimeric, with the two Ag ions in different coordination environments. One Ag ion is bound strongly to a pyridine N atom [Ag–N 2.368 (6) Å], to three O atoms in a polyether chain [Ag–O 2.397 (6) to 2.604 (8) Å] and to one S atom [Ag–S 2.501 (3) Å]. The other S atom is directed away from the macro-

cyclic cavity and is bound to the second Ag ion. This Ag ion is bound more weakly to a pyridine N atom [Ag–N 2.528 (8) Å], to three S atoms [Ag–S 2.545 (2) to 2.611 (3) Å]; there is also a weak interaction with an ether O atom [Ag–O 2.883 (7) Å]. The solution NMR data are interpreted in terms of a monomeric structure in which either the pyridine N and two S atoms are not bound simultaneously or in which the polyether chain is conformationally mobile.

Introduction. During the course of studies directed towards an examination of the binding properties of

transition-metal cations by polydentate macrocyclic ligands (Parker, Lehn & Rimmer, 1985; Alberts, Lehn & Parker, 1985; Parker, 1985; Ferguson, Langrick, Matthes & Parker, 1985; Ferguson, Matthes & Parker, 1987*a,b*), we have examined the structure of the silver complex of 6,9,12-trioxa-3,15-dithia-21-azabicyclo-[15.3.1]henicosa-1(21),17,19-triene (*L*) both in the solid state and in solution. The ligand contains two thioether donors and, in recent work, the tendency of S atoms in macrocycles to adopt exodentate conformations, with the lone pairs directed away from the macrocyclic cavity, has been highlighted (Wolf, Hartman, Storey, Foxman & Cooper, 1987; DeSimone & Glick, 1975, 1976). In the copper (Weber, 1982) and rhodium-carbonyl (Ferguson, Matthes & Parker, 1987*a*) complexes of *L*, the S atoms are exocyclic with the polyether chain being folded away from the metal centre, and back toward the electron-poor pyridine ring. In contrast, in the barium complex of *L* (Weber, 1982), the six donor lone pairs are focused towards the centre of the cavity and both S atoms are accordingly endocyclic.



Macrocyclic complexes of silver(I) are quite common (Parker & Matthes, 1987) and many examples exist in which the silver is five, six, seven or eight coordinate (Drew, McFall, Nelson & Bin Othman, 1977; Jones, Gries, Grutzmacher, Roesky, Schimkowiak & Sheldrick, 1984; Campbell & Dalley, 1981; Drew, Rice & Silong, 1984; Ferguson, McCrindle & Parvez, 1984). Although complexes of silver(I) may be expected to be non-directional, there are a large number adopting square-pyramidal or pentagonal-pyramidal coordination geometries. The crystal and molecular structure of the silver complex of *L* is reported, and its solution structure and stability have been examined by ¹H and ¹³C NMR and ion-selective electrode methods.

Experimental. Reactions were carried out under a nitrogen atmosphere using standard Schlenck techniques. Commercial solvents were distilled from an appropriate drying agent prior to use according to standard procedures. Proton NMR spectra were recorded on a Bruker AC 250 (250 MHz); ¹³C spectra were recorded on a Bruker AC 250 (62.9 MHz). Chemical shifts are given in p.p.m. relative to Me₄Si (0 p.p.m.).

Infrared spectra were recorded as KBr discs using a Perkin-Elmer 297 spectrometer. Mass spectra were recorded on a VG 7070 E spectrometer, with fast atom bombardment (f.a.b.) spectra recorded in the positive ion mode using either a glycerol or 3-nitrobenzyl alcohol as a matrix, with xenon atoms at 8 keV. Stability constants were recorded in anhydrous methanol (0.05 M in Et₄NClO₄) using an Ag-ion electrode (298 K). The ligand (*L*) was prepared following a modification of the method of Weber & Vogtle (1976) (Matthes, 1987).

Synthesis of [L-Ag]₂[PF₆]₂ (1). To a solution of the ligand *L* (23.5 mg, 0.0669 mmol) in dry dichloromethane (1.0 cm³) was added a solution of silver nitrate (11.4 mg, 0.067 mmol) in acetonitrile (1 ml). The mixture was allowed to stand (1 h) and solvent was recovered under reduced pressure to yield a colourless residue which was redissolved in methanol (1.0 cm³). To this solution was added a solution of ammonium hexafluorophosphate (24 mg, 0.134 mmol) in methanol (1.0 cm³) and the solvent was allowed to evaporate slowly depositing colourless crystals, 33 mg (85%). δ_H [250 MHz, (CD₃)₂CO] 7.87 (1H, t, J7.6), 7.47 (2H, d), 4.19 (4H, s, pyCH₂S), 3.79 (4H, t, J5.2), 3.75 (8H, s, CH₂O), 3.10 (4H, t, J5.2, CH₂S); *m/e* (f.a.b., glycerol matrix) 438, 436 [L-Ag]⁺; δ_C (62.9 MHz, CDCl₃) 34.1, 37.5 (CH₂S); 66.7, 69.8 (CH₂O); 123.8, 155.3; compare with free *L*, δ (62.9 MHz, CDCl₃) 30.1, 37.6 (CH₂S); 70.2, 70.8 (CH₂O); 121.1, 137.7, 158.4.

X-ray analysis of (1). Colourless plate crystals were grown from methanol. Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $8 < \theta < 12^\circ$. Crystal dimensions 0.18 × 0.25 × 0.30 mm; intensities of reflections with indices $h - 30$ to 30 , $k 0$ to 23 , $l 0$ to 12 , with $2 < 2\theta < 48^\circ$ measured; $\omega - 2\theta$ scans; ω -scan width (0.60 + 0.35 tan θ) graphite-monochromatized Mo K α radiation. Intensities of three reflections were measured every 2 h and showed no evidence of crystal decay. 7496 reflections were measured, 6651 were unique, and 3688 with $I > 3\sigma(I)$ were labelled observed and used in structure solution and refinement; $R_{int} = 0.018$. Data were corrected for Lorentz, polarization and absorption effects (max. and min. transmission factors 0.837, 0.798), Gaussian integration, grid 8 × 10 × 10. Space group *P2₁/n* uniquely from systematic absences $h0l$, $h+l = 2n+1$; $0k0$, $k = 2n+1$. The coordinates of the two Ag atoms were determined from an analysis of the three-dimensional Patterson function and the coordinates of the remaining non-H atoms found *via* the heavy-atom method. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. At an intermediate stage in the refinement, difference maps showed maxima in

Table 1. Positional and thermal parameters and *e.s.d.*'s

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}† (\text{Å}^2)$
Ag1	-0.05753 (3)	0.26287 (4)	-0.13113 (6)	4.37 (1)
N1A	0.0163 (3)	0.2976 (3)	0.0407 (6)	3.7 (1)
C2A	0.0715 (3)	0.2965 (4)	0.0227 (7)	3.6 (2)
C3A	0.1124 (4)	0.3285 (5)	0.1134 (9)	4.9 (2)
C4A	0.0953 (4)	0.3644 (5)	0.2252 (9)	5.6 (2)
C5A	0.0386 (4)	0.3670 (4)	0.2431 (8)	4.9 (2)
C6A	0.0001 (4)	0.3321 (4)	0.1499 (7)	4.0 (2)
C7A	-0.0613 (4)	0.3285 (5)	0.1800 (8)	5.1 (2)
S8A	-0.1167 (1)	0.3199 (2)	0.0368 (3)	5.92 (6)
C9A	-0.1254 (6)	0.4074 (6)	-0.0248 (11)	10.2 (3)
C10A	-0.0762 (7)	0.4370 (6)	-0.0905 (11)	11.2 (5)
O11A	-0.0559 (5)	0.3972 (4)	-0.2005 (7)	13.0 (3)
C12A	-0.0757 (6)	0.4055 (6)	-0.3228 (11)	9.5 (4)
C13A	-0.0612 (5)	0.3559 (6)	-0.4267 (9)	6.8 (3)
O14A	-0.0680 (3)	0.2847 (3)	-0.3830 (6)	5.8 (2)
C15A	-0.0427 (4)	0.2332 (6)	-0.4627 (9)	6.8 (3)
C16A	-0.0434 (4)	0.1634 (5)	-0.3934 (9)	6.4 (2)
O17A	-0.0164 (3)	0.1696 (3)	-0.2570 (6)	5.4 (1)
C18A	0.0001 (4)	0.1045 (5)	-0.1870 (8)	4.9 (2)
C19A	0.0364 (4)	0.1232 (4)	-0.0569 (8)	4.7 (2)
S20A	0.10320 (9)	0.1639 (1)	-0.0815 (2)	4.22 (5)
C21A	0.0876 (3)	0.2585 (4)	-0.1054 (7)	3.8 (2)
Ag2	0.15863 (3)	0.15460 (4)	0.15814 (7)	5.55 (2)
N1B	0.1692 (3)	0.0395 (4)	0.2951 (8)	5.9 (2)
C2B	0.1486 (4)	0.0425 (6)	0.4157 (10)	7.0 (3)
C3B	0.1779 (6)	0.0113 (6)	0.5339 (11)	9.2 (3)
C4B	0.2279 (6)	-0.0192 (6)	0.5282 (11)	9.3 (3)
C5B	0.2490 (5)	-0.0227 (5)	0.4026 (11)	7.1 (3)
C6B	0.2184 (4)	0.0077 (5)	0.2884 (9)	5.7 (2)
C7B	0.2389 (4)	0.0064 (5)	0.1483 (11)	5.7 (3)
S8B	0.2530 (1)	0.0973 (1)	0.0951 (3)	5.22 (6)
C9B	0.2471 (4)	0.0850 (5)	-0.0889 (9)	5.5 (2)
C10B	0.2677 (4)	0.1507 (6)	-0.1572 (9)	6.6 (3)
O11B	0.2317 (3)	0.2095 (4)	-0.1314 (6)	6.2 (2)
C12B	0.2590 (4)	0.2777 (6)	-0.1233 (10)	6.7 (3)
C13B	0.2930 (4)	0.2902 (6)	0.0091 (12)	6.9 (3)
O14B	0.2575 (3)	0.2932 (3)	0.1195 (6)	6.0 (2)
C15B	0.2896 (5)	0.2962 (6)	0.2490 (11)	7.3 (3)
C16B	0.2545 (5)	0.2977 (7)	0.3612 (11)	8.8 (3)
O17B	0.2225 (4)	0.2377 (4)	0.3719 (7)	9.8 (2)
C18B	0.2101 (9)	0.2100 (11)	0.4871 (20)	7.1 (6)
C18B*	0.1822 (12)	0.2597 (12)	0.4894 (19)	9.1 (7)
C19B	0.1509 (8)	0.2098 (9)	0.5032 (12)	13.0 (5)
S20B	0.0998 (1)	0.1754 (2)	0.3672 (3)	8.09 (8)
C21B	0.0958 (5)	0.0846 (8)	0.4212 (11)	9.6 (4)
P1	0.1157 (1)	0.4457 (1)	0.6676 (2)	4.98 (6)
F11	0.1377 (4)	0.4531 (4)	0.5247 (6)	11.8 (2)
F12	0.0895 (3)	0.3713 (3)	0.6286 (8)	11.1 (2)
F13	0.0916 (4)	0.4388 (4)	0.8068 (6)	14.1 (3)
F14	0.1403 (3)	0.5214 (3)	0.7069 (7)	11.6 (2)
F15	0.1703 (4)	0.4120 (5)	0.7192 (11)	17.1 (3)
F16	0.0595 (3)	0.4816 (5)	0.6112 (11)	16.2 (3)
P2	0.4033 (1)	0.4069 (2)	0.6736 (3)	6.68 (7)
F21	0.4495 (4)	0.3468 (4)	0.6968 (9)	14.4 (3)
F22	0.4185 (5)	0.4305 (6)	0.8214 (7)	19.3 (3)
F23	0.3673 (4)	0.4707 (5)	0.6577 (9)	19.4 (3)
F24	0.3893 (4)	0.3772 (6)	0.5235 (8)	15.8 (3)
F25	0.4529 (4)	0.4492 (4)	0.6187 (10)	16.6 (3)
F26	0.3612 (4)	0.3665 (7)	0.7299 (12)	27.5 (4)

* Atoms C18B and C18B* are disordered sites for C18 in molecule B; they were included with 0.5 occupancy.

† Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + abc\cos\gamma B_{12} + acc\cos\beta B_{13} + bcc\cos\alpha B_{23}]$$

positions consistent with the expected locations of the H atoms; in the final rounds of calculations the H atoms were positioned on geometrical grounds (C—H 0.95 Å) and included (as riding atoms) in the structure-factor calculations with an overall B_{iso} of 5.0 Å². During the refinement, one of the atoms (C18B) developed markedly anisotropic thermal parameters (U_{ii} in the range 0.06 to 0.39 Å²). A separate refinement with C18B allowed for as two disordered half atoms converged with essentially the same R and wR as found for the non-disordered model. There were no sig-

Table 2. Principal molecular dimensions (Å, °)

Ag1	N1A	2.368 (6)	Ag2	S20A	2.545 (2)		
Ag1	S8A	2.501 (3)	Ag2	N1B	2.528 (8)		
Ag1	O11A	2.604 (8)	Ag2	S8B	2.611 (3)		
Ag1	O14A	2.460 (5)	Ag2	O17B	2.883 (7)		
Ag1	O17A	2.397 (6)	Ag2	S20B	2.610 (3)		
S8A	C7A	1.809 (8)	S8B	C7B	1.821 (10)		
S8A	C9A	1.747 (12)	S8B	C9B	1.788 (9)		
S20A	C19A	1.796 (9)	S20B	C19B	1.807 (14)		
S20A	C21A	1.819 (8)	S20B	C21B	1.783 (14)		
N1A	Ag1	S8A	81.3 (2)	S20A	Ag2	N1B	123.3 (2)
N1A	Ag1	O11A	83.4 (3)	S20A	Ag2	S8B	100.57 (8)
N1A	Ag1	O14A	129.6 (2)	S20A	Ag2	O17B	142.8 (2)
N1A	Ag1	O17A	104.3 (2)	S20A	Ag2	S20B	115.62 (8)
S8A	Ag1	O11A	77.4 (2)	N1B	Ag2	S8B	74.7 (2)
S8A	Ag1	O14A	124.9 (2)	N1B	Ag2	O17B	94.0 (2)
S8A	Ag1	O17A	158.5 (2)	N1B	Ag2	S20B	75.5 (2)
O11A	Ag1	O14A	65.6 (2)	S8B	Ag2	O17B	89.7 (2)
O11A	Ag1	O17A	123.6 (3)	S8B	Ag2	S20B	115.62 (9)
O14A	Ag1	O17A	67.6 (2)	O17B	Ag2	S20B	69.2 (2)
Ag1	S8A	C7A	97.2 (3)	Ag2	S8B	C7B	97.4 (4)
Ag1	S8A	C9A	103.4 (4)	Ag2	S8B	C9B	108.1 (3)
C7A	S8A	C9A	103.1 (5)	C7B	S8B	C9B	99.5 (5)
C19A	S20A	C21A	105.1 (4)	Ag2	S20B	C19B	104.3 (5)
C19A	S20A	Ag2	102.9 (3)	Ag2	S20B	C21B	97.8 (4)
C21A	S20A	Ag2	105.1 (2)	C19B	S20B	C21B	100.3 (6)

nificant differences in molecular dimensions (apart from those involving C18B) between the two refinements; the data reported below are for the disordered model. The final cycle of refinement included 532 variable parameters, $R = 0.045$, $wR = 0.058$, goodness-of-fit 1.76, $w = 1/[\sigma^2(F_o) + 0.050(F_o)^2]$. Maximum coordinate shift/*e.s.d.* = 0.07; density in final difference map $\pm 0.88 \text{ e Å}^{-3}$ adjacent to Ag atoms; no chemically significant features. Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a PDP11/73 computer using *SDP-Plus* (B. A. Frenz & Associates Inc., 1983). Atomic coordinates and details of molecular geometry are given in Tables 1 and 2.* Fig. 1, prepared using *ORTEPII* (Johnson, 1976), shows details of the cation structure and silver coordination.

Discussion. Reaction of silver nitrate and *L* in equimolar amounts in dichloromethane–acetonitrile (1:1) led to formation of the silver complex, (1), which was isolated as the hexafluorophosphate salt from methanol. In the ¹H NMR spectrum of (1) [²H₆acetone], the benzylic methylene protons resonated as a singlet which broadened ($\omega_{\frac{1}{2}}$ 60 Hz, 203 K) at lower temperature as did the eight methylene protons of the polyether chain [OCH₂CH₂OCH₂CH₂O]. The ¹³C NMR spectrum of (1) also indicated that the complex – on the NMR timescale – possessed the same symmetry as the free ligand *L*. Such behaviour is in accord with a

* Lists of structure factors, thermal parameters, calculated H-atom coordinates, and all bond lengths, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51632 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

structure in solution in which either the pyridine N and the two S atoms are not bound simultaneously or in which the polyether chain is conformationally mobile permitting the rapid inversion of the sulfur centres and

thereby rendering the geminal methylene benzylic protons isochronous. The complex is relatively stable, compared with other silver macrocyclic complexes (Izatt, Bradshaw, Nielson, Lamb, Christensen & Sen, 1985; Louis, Arnaud-Neu, Weiss & Schwing-Weil, 1977; Louis, Agnus & Weiss, 1977), and a stability constant, $\log K$, of 8.83 was measured in anhydrous methanol (298K, $I=0.1$) using an Ag-ion electrode. The fast atom bombardment mass spectrum of (1) gave peaks at 438, 436, consistent with formation of a mononuclear complex in the glycerol matrix.

The crystal structure of (1) revealed that the complex was dimeric in the solid state, with the two Ag ions having distinctly different coordination environments. One Ag ion is bound strongly to the pyridine N atom [Ag1-N1A 2.368 (6) Å], to the three O atoms [Ag1-O11A 2.604 (8), Ag1-O14A 2.460 (5), Ag1-O17A 2.397 (6) Å] in the polyether chain and to one S atom [Ag1-S8A 2.501 (3) Å]. The other S atom in the macrocycle is directed away from the macrocyclic cavity and is bound to a second Ag ion [Ag2-S20A 2.545 (2) Å], thereby constituting the bridge in this dimeric structure (Fig. 1). The second Ag ion is bound more weakly to the pyridine N atom [Ag2-N1B 2.528 (8) Å], but is coordinated to both S atoms of the second macrocycle [Ag2-S8B 2.611 (3), Ag2-S20B 2.610 (3) Å]; there is also a weak cation-dipole interaction with one O atom [Ag2-O17B 2.883 (7) Å]. It is evident that simultaneous coordination of the pyridine N atom, the two S atoms and any O atom in the polyether chain leads to a rather strained conformation for the complex, as evidenced by the rather obtuse S8B-Ag2-S20B bond angle of 141.82 (9)° [cf. 169.8 and 165.1° in the five-coordinate rhodium-carbonyl (Ferguson, Matthes & Parker, 1987a) and copper(II) chloride (Weber, 1982) complexes of *L*], the long Ag2-N1B bond length [2.528 (8) Å], and some of the torsional angles in the silver complex showing large disparities from the idealized strain-free values of 180° (*trans*) for C-X-C-C and $\pm 60^\circ$ (*gauche*) for X-C-C-X.

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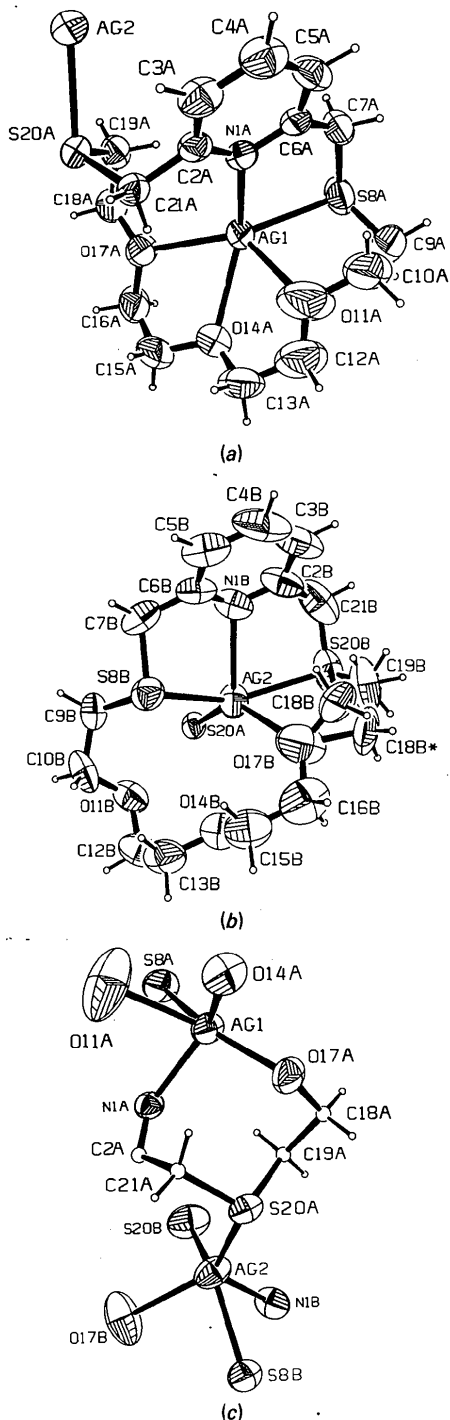


Fig. 1. (a), (b) Views of the two macrocyclic ring systems in (1); atoms labelled C18B and C18B* are the two disordered sites for C18B. (c) The coordination environment around each Ag ion in (1). Ellipsoids are at the 50% level.

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Transition-Metal Complexes with Thiosemicarbazide-Based Ligands. VIII. Structure of Ammine(benzoylacetone *S*-methylisothiosemicarbazonato)nickel(II) Iodide

BY N. GALEŠIĆ

'Rudjer Bošković' Institute, POB 1016, 41001 Zagreb, Yugoslavia

AND V. M. LEOVAC

Institute of Chemistry, Faculty of Sciences, V. Vlahovića 2, 21000 Novi Sad, Yugoslavia

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Abstract. $[\text{Ni}(\text{C}_{12}\text{H}_{14}\text{N}_3\text{OS})(\text{NH}_3)]\text{I}$, $M_r = 450.96$, monoclinic, $P2_1/c$, $a = 6.198$ (2), $b = 17.401$ (5), $c = 15.343$ (4) Å, $\beta = 96.54$ (3)°, $V = 1644.0$ (8) Å³, $Z = 4$, $D_m = 1.81$, $D_x = 1.822$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 31.66$ cm⁻¹, $F(000) = 888$, $T = 293$ K, final $R = 0.038$ for 1804 observed reflections. The Ni coordination environment is a slightly distorted square determined by the O, N(1) and N(4) atoms from the terdentate ligand and the ammonia N atom with corresponding bond lengths of 1.817 (5), 1.824 (6), 1.847 (6) and 1.918 (6) Å, respectively. The complex cation shows deviations of its non-H atoms within ± 0.32 (1) Å from planarity. All nitrogen H atoms are involved in weak N–H...I hydrogen bonds ranging from 3.609 (6) to 3.841 (7) Å.

Introduction. The synthesis and structural investigations of a considerable number of transition-metal complexes with *S*-alkylisothiosemicarbazides and *S*-alkylisothiosemicarbazones have recently been reported (Padhye & Kauffman, 1985, and references therein; Leovac, Divjaković, Petrović, Argay & Kálmán, 1983,

and references therein; Leovac & Češljević, 1987). A common feature of the complexes is that the N atom of the *S*-alkylthioamido group takes part in coordination, while the S atom remains uncoordinated.

As far as the authors are aware only two exceptions have been noticed. Biyushkin, Gerasimov & Rozhdestvenskaya (1986) reported the structure of an Ni^{III} complex with chlorine and diacetylmonoxime *S*-methylisothiosemicarbazone where Ni is coordinated by N atoms of hydrazine and oxime and by chlorine, while neither N nor S atoms from the *S*-methylthioamido group take part in the coordination. Chandra & Singh (1986) supposed that thiosemicarbazones of acetone and methyl ethyl ketone, coordinated to the Ni^{II} atom through S and hydrazine N atoms, do not change the coordinating atoms after alkylation of the S atom.

In the crystal structure of the $[\text{Ni}(\text{HL})(\text{NH}_3)]\text{I}$ complex, where HL is $\text{C}_6\text{H}_5\text{C}(\text{O})=\text{CHC}(\text{CH}_3)=\text{NNHC}(\text{SCH}_3)=\text{NH}$, the *S*-methylthioamido group is attached to the Ni^{II} by an N atom, thus showing the usual mode of metal coordination.