

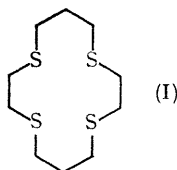
Metal Complexes of a Quadridentate Macrocyclic with only Sulphur Donor Atoms

By WILLIAM ROSEN and DARYLE H. BUSCH*

(The Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210)

METAL complexes with a macrocyclic quadridentate ligand in the equatorial plane of a metal ion have been described;¹ the majority have four nitrogens as the donor atoms of the macrocycle. We report an example of a quadridentate macrocyclic ligand with sulphur atoms as the only donors; some of the properties of its metal ion complexes.

The ligand, 1,4,8,11-tetrathiacyclotetradecane (tc) (I), was synthesized from propane-1,3-dithiol, by a modification of the procedure of Reid and his co-workers.² The final step of the sequence involves the reaction of the dianion of 1,4,8,11-tetrathiaundecane with 1,3-dibromopropane, to produce (I) (m.p. 119–120), mass spectrum $m/e = 268 (M)$, n.m.r. τ 7.25 (overlapping s and t, area 16) and 8.02 (quint., area 4).



Reaction of (I) with the hexa-acetic acid derivative of nickel(II) tetrafluoroborate³ in nitromethane gave the reddish orange Ni tc (BF₄)₂, which is soluble in nitromethane but reacts with water EtOH, and Me₂SO, as do all the complexes prepared, to give free (I) and the solvated nickel(II) ion.

Diamagnetic Ni tc (BF₄)₂ also reacts with anions in nitromethane-acetone to produce the paramagnetic thiocyanate, chloride, bromide, and iodide and the diamagnetic perchlorate. Physical data for the salts are summarized in the Table.

As indicated, the thiocyanate, chloride, and bromide are paramagnetic nonelectrolytes. From their spectra a Dq_{xy} value¹ of 1070 cm.⁻¹ is calculated for (I) on nickel(II). The tetrafluoroborate and perchlorate, however, are diamagnetic 2 : 1 electrolytes with spectra typical of square-planar species

and are the first examples of low-spin nickel(II) with four sulphide linkages as the donors.[†]

The iodide is on the border line where the six-co-ordinate, high-spin species is very similar in stability to the low-spin species of reduced co-ordination number. In the solid state it is paramagnetic and shows spectra typical of six-co-ordinate nickel(II). However, in nitromethane solution the spectrum is unlike that of any of the other complexes and the molar conductance of the solute is concentration-dependent. Two successive equilibria are implicated in these solutions as shown in the Figure. At low concentration a 2 : 1 and a 1 : 1

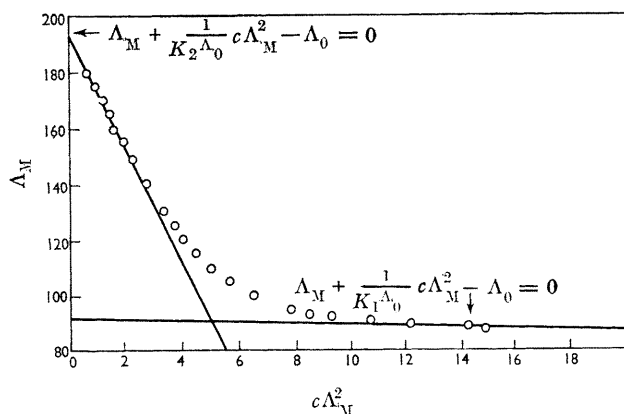


FIGURE. Graphical demonstration that Ni tc I₂ solutions in nitromethane undergo two successive electrolytic dissociations; Λ_M = molar conductance at the concentration c , Λ_0 = molar conductance at infinite dilution. K_1 and K_2 are the successive ionization constants.

electrolyte are in equilibrium, while at higher concentration the 1 : 1 electrolyte is in equilibrium with a nonelectrolyte. Obviously all these species exist over a broad range of

Properties of the new complexes, Ni tc X₂

Property	X	BF ₄	ClO ₄	I	Br	Cl	NCS
μ_{eff} (B.M.)		d ^a	d ^a	3.10	3.18	3.04 ^c	3.11
Λ_M (mho-cm. ²) mole		194	189	b	18.1	23.9	27.7
λ_{max} (MeNO ₂) (cm. ⁻¹)		20,400 [ε263] 24,090 [98]	20,320 [270] 23,810 [100]	14,290 [58] 18,520 [315]	9,010 [16] 10,640 [48] 16,390 [53]	9,260 [25] 10,640 [48] 16,390 [28]	9,900 [34] 10,930 [54] 17,540 [28]
λ_{max} (solid) (cm. ⁻¹)			20,410 24,390 31,250	8,260 10,990 16,530 26,320	8,930 10,990 16,950 29,410	9,170 11,110 16,950 29,410	9,990 11,110 17,540 28,570

^a Diamagnetic.

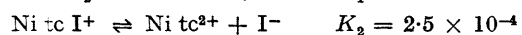
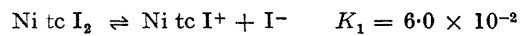
^b Concentration dependent, see text.

^c Obtained from n.m.r. measurements (D. F. Evans, *J. Chem. Soc.*, 1959, 2003).

[†] The n.m.r. spectrum of 1,4,8,11-tetra-azacyclotetradecane (B. Bosnich, C. K. Poon and M. L. Tobe, *Inorg. Chem.*, 1965, 4, 1102, 1109) displays similar overlapping patterns composed of a singlet and a triplet at τ 7.25, area 16, and a quintuplet at τ 8.25, area 4.

[‡] The proton n.m.r. spectrum of Ni tc (BF₄)₂ displays a broad multiplet between τ 5.9 and 8.0 whose pattern is very similar to that displayed for Ni(N-D₄-cyclam)(ClO₄)₂ indicating that the configuration of the organic ligands are analogous.

intermediate concentrations. The equilibrium constants calculated for the processes are:⁴



We thank the National Institutes of Health, U.S. Public Health Service, for financial support.

(Received, December 16th, 1968; Com. 1716.)

¹ D. H. Busch, *Helv. Chim. Acta, Special Issue*, 1967, 174.

² N. B. Tucker and E. E. Reid, *J. Amer. Chem. Soc.*, 1933, **55**, 775; A. M. Reeves and E. E. Reid, *Amer. Chem. Soc., San Francisco Meeting Abstracts*, 1949 65L.

³ P. W. N. M. van Leeuwen and W. L. Groenveld, *Rec. Trav. chim.*, 1968, **87**, 86.

⁴ L. Sacconi, P. Nannelli, N. Nardi, and V. Campigli, *Inorg. Chem.*, 1965, **4**, 943.