

631. The ^{14}N Chemical Shifts in Metal-Thiocyanate Complexes.

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The ^{14}N chemical shifts have been used to determine whether the thiocyanate ligand is bonded to the metal atom through sulphur or through nitrogen in soluble, diamagnetic complexes.

THE thiocyanate ion can act as a ligand in a mononuclear complex by bonding either through its nitrogen atom or through its sulphur atom. A reliable structural distinction has been made in many cases by X-ray crystallography and by infrared spectroscopy.¹ This Paper describes a complementary method of structural distinction, using nuclear magnetic resonance.

The nucleus ^{14}N has a spin of one, and hence an electric quadrupole moment which broadens its resonance signals considerably when the electric field at the nucleus is unsymmetrical. Thus, ^{14}N line-widths in solution vary from 0.02 gauss in the nitrate ion to more than 20 gauss in organic amines, and in diamagnetic thiocyanate complexes vary from 0.5 to 5 gauss. The widest of these lines can just be measured reproducibly on the spectrometer used, provided that a very strong solution of the complex can be made. With the favourable compounds chosen, it was possible to measure the ^{14}N chemical shifts with sufficient accuracy to distinguish between the different nuclear environments associated with metal-nitrogen and metal-sulphur bonding.

EXPERIMENTAL AND RESULTS

Measurements were made on a Varian 4200B Wide Line Spectrometer, at a frequency of 3900 kc./sec. and a magnetic field of *ca.* 12,680 gauss. The radio-frequency field was as high as could be permitted without significantly heating the sample, and the field-modulation amplitude was about half the line-width in gauss. Shifts were measured relative to the nitrate resonance in molar ammonium nitrate, using a frequency-sweep method with the magnetic field held constant by means of a flux-stabiliser. The frequency was monitored by means of a counter, and could be measured to 1 c./sec. The accuracy of the chemical-shift measurements depends on the line-widths, and was always better than ± 5 p.p.m. The shifts were independent of concentration, within the experimental error.

Ultraviolet spectra were recorded on a Unicam S.P. 700 spectrophotometer, and infrared spectra on a Perkin-Elmer 221 spectrophotometer fitted with a caesium bromide prism.

All complexes were prepared by standard methods, except for that of ruthenium, which was previously unreported.

Dipotassium Pentaisothiocyanatonitrosylruthenium $\text{K}_2[\text{Ru}(\text{NCS})_5(\text{NO})]$.—This complex was prepared by heating dipotassium pentachloronitrosylruthenium (1.5 g.) with potassium thiocyanate (2.0 g.). It was extremely soluble in water and very hygroscopic, and was therefore difficult to obtain analytically pure. However, its *benzyltriphenylphosphonium analogue* was prepared by extraction of an aqueous solution of the potassium compound with methylene chloride containing benzyltriphenylphosphonium chloride (2.5 g.), followed by repeated washing of the organic layer with water, and final crystallisation of the red-brown solid by addition of tetrahydrofuran and slow partial evaporation (Found: C, 57.8; H, 3.8; N, 7.5; P, 4.4. $\text{C}_{55}\text{H}_{44}\text{N}_6\text{O}_2\text{P}_2\text{RuS}_5$ requires C, 58.5; H, 3.8; N, 7.1; P, 4.5%).

Results.—The ^{14}N chemical shifts, together with the approximate line-widths, for the thiocyanate complexes are given in the Table. Positive shifts indicate that the resonance occurs at a higher applied field than does the nitrate resonance.

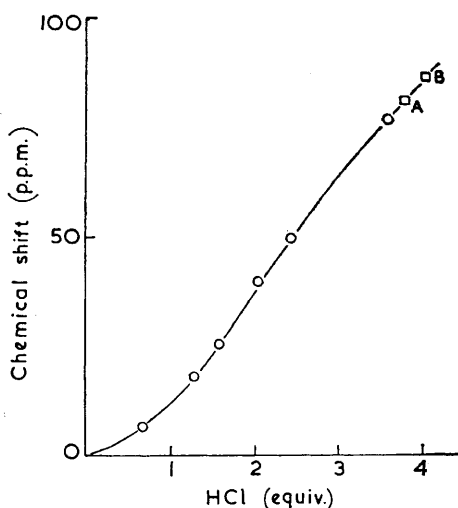
The ultraviolet spectra for some of the complexes were measured, the following absorption bands (in cm^{-1}) being observed: (I) 44,500; (I), with added trace of Co^{2+} , Ni^{2+} , Fe^{3+} , or Cd^{2+} , 35,000—36,000; (II) 41,300, 34,300, 23,500; (III) 37,000, 32,500, 20,700; (V) 34,800; (VI) 45,000, 35,300; (VIII) 42,500, 35,800; (IX) 38,300; (X) 38,300, 32,800; (XI) 40,300, 35,700, 29,800; (XII) 41,000, 36,600, 33,400, 28,000; (XIII) 39,700, 33,000, 26,500; (XVII) 44,500, 40,700, 36,200, 29,400. (See Discussion section for significance of figures in italics.) Extinction coefficients were of the order of 10^3 — 10^4 .

¹ Lewis, Nyholm, and Smith, *J.*, 1961, 4590, and previous references quoted therein.

^{14}N Chemical shifts, δ (p.p.m.), and approximate line-width (gauss) in thiocyanate complexes.

	$\delta_{\text{NO}_3^-}$	δ_{KSCN}	Approx. line-width	Solvent
(I) KSCN (pH 4.5)	+166	—	0.05	H_2O
(II) $\text{Na}_2[\text{Pd}(\text{SCN})_4]$	+148	-18	2	H_2O
(III) $\text{K}_2[\text{Pt}(\text{SCN})_4]$	+166	0	0.5	H_2O
(IV) $\text{K}_3[\text{Rh}(\text{SCN})_6]$	+158	-8	2	H_2O
(V) $\text{Na}_3[\text{Ir}(\text{SCN})_6]$	+163	-3	0.5	H_2O
(VI) $\text{Na}_2[\text{Hg}(\text{SCN})_4]$	+157	-9	1	H_2O
(VII) $\text{C}_2\text{H}_5\text{SCN}$	+98.5	-67.5	0.5	CHCl_3
(VIII) <i>cis</i> - $[\text{Pt}(\text{NCS})_2(\text{Bu}_3\text{P})_2]$	+302	+136	3	CHCl_3
(IX) <i>cis</i> - $[\text{Pt}(\text{NCS})_2(\text{Bu}_2\text{PhP})_2]$	+249	+83	3	CHCl_3
(X) <i>trans</i> - $[\text{PtH}(\text{NCS})(\text{Et}_3\text{P})_2]$	+239	+73	1.5	CHCl_3
(XI) <i>cis</i> - $[\text{Pt}(\text{NCS})_2(\text{Bu}_3\text{As})_2]$	+303	+137	2	CHCl_3
(XII) <i>trans</i> - $[\text{Ni}(\text{NCS})_2(\text{Et}_3\text{P})_2]$	+293	+127	1	CHCl_3
(XIII) <i>trans</i> - $[\text{Ni}(\text{NCS})_2(\text{Bu}_2\text{PhP})_2]$	+291	+125	1	CHCl_3
(XIV) $\text{Na}_2[\text{Cd}(\text{NCS})_4]$	+178	+12	0.5	H_2O
(XV) $\text{Na}_2[\text{Cd}(\text{NCS})_4]$	+220	+54	3	MeOH
(XVI) $\text{Na}_2[\text{Zn}(\text{NCS})_4]$	+255.5	+59.5	1	EtOH
(XVII) $\text{K}_3[\text{Ru}(\text{NCS})_5(\text{NO})]$	+245	+79	1	H_2O
(XVIII) $\text{C}_2\text{H}_5\text{NCS}$	+268	+102	0.5	(Pure)

The chemical shift of the ^{14}N resonance of 4.13M-aqueous potassium thiocyanate was studied as a function of the concentration of added hydrochloric acid. The results are summarised in the Figure; also shown are the chemical shift of 0.30 ml. of 60% HClO_4 + 0.20 g. KSCN in



Variation of ^{14}N chemical shift of aqueous solutions of potassium thiocyanate containing HCl. The abscissa gives the number of equivalents of HCl per equivalent of NCS^- , the total concentration of NCS^- being always 4.13M.

5.0 ml. of absolute alcohol (A) and of 1.20 ml. of 60% HClO_4 + 0.20 g. KSCN in 4.0 ml. of absolute alcohol (B).

The chemical shift of disodium tetrathiocyanatozinc also varied with concentration in water, but was independent of concentration in absolute alcohol.

The ^{14}N resonance of *cis*- $[\text{Pt}(\text{NCS})_2(\text{Bu}_3\text{P})_2]$ is a triplet. The central component arises from molecules containing the ^{194}Pt isotope with zero nuclear spin, and the outer components arise from molecules containing the ^{195}Pt isotope with a nuclear spin of one half. The platinum-nitrogen spin coupling constant in this compound is 430 ± 3 c./sec.

DISCUSSION

It is clear that in all the compounds known to be S-bonded complexes, namely, (II),² (III),² (IV),² (VI),² and (VII), the ^{14}N resonance is shifted slightly downfield from

² Tramer, *J. Chim. phys.*, 1962, **59**, 232; Bailar and Chamberlain, *J. Amer. Chem. Soc.*, 1959, **81**, 6412.

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that of the free thiocyanate ion. For the known N-bonded complexes (X),³ (XII),⁴ (XV),⁵ and (VIII), and for (VIII), (IX), and (XI), which are likely to be N-bonded by analogy with $[\text{Pt}(\text{NCS})_2(\text{Et}_3\text{P})_2]$ and $[\text{Pt}(\text{NCS})_2(\text{Pr}^i_3\text{P})_2]$, it is shifted by a comparatively large amount upfield from that of the free thiocyanate ion. This establishes a new and reliable means of structural differentiation, and is confirmed by infrared measurements on compounds (V), (VIII), (IX), and (XIII), which show C-S stretching vibrations at 700, 853, 848, and 859 cm^{-1} , respectively.

It is interesting that the thiocyanate group in $\text{K}_2[\text{Ru}(\text{NCS})_5(\text{NO})]$ is N-bonded. Evidently, the effect of the NO^+ ligand on the ruthenium atom is analogous to that of the phosphine and arsine ligands on platinum and palladium.⁶

The shifts of disodium tetrathiocyanatocadmium are independent of concentration, showing that the complex is not very labile. The very large solvent effect must, therefore, be attributed to the existence in solution of both N- and S-bonded species in kinetic equilibrium. The more polarisable N-bonded form would be favoured by the less polar solvent. This result is supported, but not firmly established, by both X-ray-diffraction⁵ and Raman-spectroscopic⁷ studies.

The results from solutions containing thiocyanic acid show that the main tautomer present must be HNCS, in accordance with microwave measurements on the vapour.⁸ It is also clear that the acid is appreciably dissociated in aqueous and in aqueous ethanolic solution. The chemical shift of the ^{14}N resonance of the pure acid must be in the region of +100 to +150 p.p.m., with respect to thiocyanate ion. The results could not be used to obtain satisfactory $\text{p}K$ values for this acid, because at the concentrations used, activity coefficients were far from unity, and were not known.

The spin-spin coupling constant of 430 c./sec. between platinum and nitrogen is the only value known for these two atoms. It may be compared with values of 2 to 6 kc./sec. for Pt-P coupling constants.⁹

The chemical shift of the nitrogen resonance is very probably caused mainly by changes in the temperature-independent paramagnetism.¹⁰ For a related set of molecules, this can often be correlated with the appropriate electronic energy levels,¹¹ and for nitrogen the most relevant transition is likely to be the $n-\pi^*$ transition of the lone-pair electrons of the nitrogen atom. Unfortunately, there does not appear to be any published assignment of the spectra of these complexes. However, it is possible to make just one arbitrary choice of one transition of each compound which gives the required relationship between chemical shift and wavelength. The bands chosen for this purpose are shown in italics in the Results section. They are all weakly forbidden ones ($\epsilon \approx 10^3$), in accordance with the non-bonding character of the orbital on the nitrogen. If these arbitrarily chosen peaks are indeed the $n-\pi^*$ transitions, it is then easy to understand how N-bonding lowers the energy of the non-bonding orbital and shifts the ^{14}N resonance upfield, and how S-bonding, while not affecting the non-bonding orbital, lowers the energy of the delocalised anti-bonding orbital by mixing in its own stabilised d -orbitals, thus causing a small low-field shift of the resonance.

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⁴ Turco and Pecile, *Nature*, 1961, **191**, 66.

⁵ Djanov and Zvonkova, Comm. 13th I.U.P.A.C. Conference, Stockholm, 1953, p. 175.

⁶ Basolo, Burmeister, and Poë, personal communication.

⁷ Plane, personal communication.

⁸ Beard and Bailey, *J. Chem. Phys.*, 1947, **15**, 762.

⁹ Pidcock, Richards, and Venanzi, *Proc. Chem. Soc.*, 1962, 184.

¹⁰ Ramsey, *Phys. Rev.*, 1950, **78**, 699.

¹¹ Freeman, Murray, and Richards, *Proc. Roy. Soc.*, 1957, *A*, **242**, 455; Figgis, Kidd, and Nyholm, *ibid.*, 1962, *A*, **269**, 469.