^{14}N Nuclear Quadrupole Resonance Spectra of Co-ordinated Thiocyanate

By C. P. CHENG and THEODORE L. BROWN
(*School of Chemical Sciences and Materials Research Laboratory, University of Illinois-Urbana, Urbana, Illinois* 61801)
and WILLIAM C. FULTZ and JOHN L. BURMEISTER
(*Department of Chemistry, University of Delaware, Newark, Delaware* 19711)

Summary The ^{14}N n.q.r. spectra have been measured for N- and S-bonded thiocyanates as ligands in several Pd^{II} complexes and a Ni^{II} complex; this technique sharply distinguishes between the two modes of bonding.

THE ambidentate bonding capability of the thiocyanate ion (NCS$^-$) has been the subject of extensive investigation.[1] A wide range of spectroscopic techniques, in addition to X-ray diffraction studies of solid-state structures, has been employed to determine whether thiocyanate is bonded to the metal through N or S. Unfortunately, spectroscopic techniques, particularly those which have been most widely applied, *e.g.*, i.r., are not without ambiguity. N.q.r. spectroscopy affords in principle an excellent means of distinguishing thiocyanate linkage isomers, since the environment about nitrogen is substantially different in the two cases. Application of the n.q.r. technique to this problem has been limited by the difficulties in obtaining low-frequency n.q.r. spectra. The double resonance level crossing technique obviates this difficulty for samples in which the proton T_1 times are sufficiently long.[2–4]

The Table lists ^{14}N n.q.r. data for several thiocyanate complexes, involving both S- and N-bonded isomers. (The four complexes involving $AsPh_3$ or PPh_3 as ligand are all *trans*.) In a few cases, the ν_- resonance, generally much less intense than ν_+,[2] was not observed. In addition ν_0 is ordinarily unobservable when it occurs below 100 kHz.

TABLE. ^{14}N N.q.r. data at 77 K.

Compound	ν_+[a]	ν_-[a]	ν_0[a]	e^2Qq/h[a]	η
$[Pd(AsPh_3)_2(SCN)_2]$	2841	2279	562	3413	0·329
$[Pd(dmp)(SCN)_2]$[b]	2570	—	420	3147	0·267
	2683	—	420	3267	0·257
$[Pd(bipy)(SCN)_2]$[c]	2787	2181	606	3312	0·366
	2764	2226	538	3327	0·323
$[Pd(phen)(SCN)_2]$[d]	2770	—	562	3319	0·339
$[Pd(nphn)(SCN)_2]$[e]	2692	—	548	3224	0·340
$[Pd(AsPh_3)_2(NCS)_2]$	301	238	—	359	0·35
$[Pd(PPh_3)_2(NCS)_2]$	298	247	—	363	0·28
$[Ni(PPh_3)_2(NCS)_2]$	405	339	—	496	0·266
$[Zn(NC_5H_5)_2(NCS)_2]$[f]	760	660	100	947	0·211
	715	615	100	887	0·266
$[Pd(dpp)(NCS)_2]$[b]	776	731	—	1005	0·090

[a] Frequencies in kHz. [b] dmp = Bis(diphenylphosphino)-methane. dpp = Bis(diphenylphosphino)propane. [c] The ^{14}N resonances due to co-ordinated 2,2′-bipyridyl (bipy) occur at 1632 and 1511 kHz; $e^2Qq/h = 2095$ kHz, $\eta = 0{\cdot}116$. [d] Ref. 4; phen = 1,10-phenanthroline. [e] nphn = 5-Nitro-1,10-phenanthroline. The ^{14}N resonances due to co-ordinated nphn occur at 1620 and 1587 kHz; $e^2Qq/h = 2138$ kHz, $\eta = 0{\cdot}031$. The signals due to the nitro-group occur at 838, 674, and 164 kHz; $e^2Qq/h = 1008$ kHz, $\eta = 0{\cdot}325$. [f] Ref. 3.

The quadrupole coupling constants, e^2Qq/h, and asymmetry parameter η, for S-bonded thiocyanate complexes are similar to those reported previously for S-bonded thiocyanate compounds.[5] The nitrogen environment is characteristic of a cyano-type nitrogen. There has been only one previous report of ^{14}N n.q.r. data for an N-bonded thiocyanate, for bis(isothiocyanato)bis(pyridine)zinc(II).[3] The new examples listed in the Table show that in closely related complexes of Pd^{II}, the N- and S-bonded complexes show substantially different field-gradient parameters.

The data shown for $[Pd(nphn)(SCN)_2]$ (nphn = 5-nitro-1,10-phenanthroline) illustrate the utility of the ^{14}N n.q.r. data as a diagnostic tool for determining thiocyanate bonding modes. The complex was first prepared as the N-bonded isomer;[6] the heretofore unknown S-bonded isomer was prepared in this study by carrying out the reaction at a higher temperature. The S-bonded mode indicated by the ^{14}N n.q.r. data is in agreement with that suggested by the i.r. data for the complex.

The field gradients at ^{14}N in the N-bonded complexes are substantially lower than those in the S-bonded compounds. In view of the large M–N–C angle in the N-bonded complexes,[1] it appears that there is no single nitrogen 2*p* orbital which is occupied largely by a lone electron pair. In the predominant resonance structures, $\mathrm{M{-}\ddot{N}{=}C{=}\ddot{S}{:}} \leftrightarrow \mathrm{M{-}N{\equiv}C{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}{:}}$, the distribution of electrons in the σ and π orbitals is apparently such that only a small net field gradient at nitrogen results. Because the population differences are small, relatively slight changes in the degree of interaction with the metal can be expected to change the field-gradient parameters substantially. Correlation of field-gradient parameters with more subtle aspects of metal–ligand bonding must await additional data and more detailed analysis. For the present, it is clear that the n.q.r. technique is capable of unambiguously distinguishing the co-ordination mode for thiocyanate. The use of n.q.r spectra of ^{14}N, and probably also of ^{17}O, should prove generally useful in determining the mode of co-ordination of ambidentate ligands in solid, diamagnetic complexes.

This research was supported by the National Science Foundation, and The Petroleum Research Fund, administered by The American Chemical Society.

(*Received*, 27*th May* 1977; *Com.* 520.)

---

[1] J. L. Burmeister, in 'Chemistry and Biochemistry of Thiocyanic Acid and its Derivatives,' ed. A. A. Newman, Academic Press, London, 1975, pp. 68—130.

[2] D. T. Edmonds, *Phys. Reports*, 1977, **29**, 233.

[3] Y. N. Hsieh, G. V. Rubenacker, C. P. Cheng, and T. L. Brown, *J. Amer. Chem. Soc.*, 1977, **99**, 1384.

[4] C. P. Cheng, B. Plankey, J. V. Rund, and T. L. Brown, *J. Amer. Chem. Soc.*, in the press.

[5] R. Ikeda, D. Nakamura, and M. Kubo, *J. Phys. Chem.*, 1966, **70**, 3626; T. Asagi, R. Ikeda, and D. Nakamura, *Z. Naturforsch.*, **1976**, **31b**, 1483.

[6] I. Bertini and A. Sabatini, *Inorg. Chem.*, 1966, **5**, 1025.