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Multinuclear NMR Studies of Electron Distributions: ^{14}N, ^{13}C, and ^{95}Mo Spectra of Nitrosyl and Thionitrosyl Complexes of Chromium, Molybdenum, and Tungsten

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Previously we have shown that ^{14}N and ^{95}Mo NMR are useful techniques for studying piano stool nitrosyl complexes such as $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$.[1] Recently a number of related nitrosyl and thionitrosyl complexes of group 6 metals have been synthesized.[2,3] The availability of new thionitrosyl complexes of the Cr, Mo, W triad has permitted us to directly compare the spectroscopic properties of several pairs of metal nitrosyl/thionitrosyl species. Here we present the first nitrogen NMR data for a thionitrosyl complex, and we demonstrate the applicability of ^{14}N NMR, particularly in combination with ^{95}Mo NMR and ^{13}C NMR, for providing specific experimental information on the relative electron distribution and bonding of nitrosyls and thionitrosyls with metals.

Experimental Section

Synthesis of Complexes. $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ (**1a**) and $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ (**1b**) were prepared according to Greenhough et al.[2] The procedure of McCleverty et al.[4] was used to prepare $HB(3,5\text{-}Me_2Pz)_3Mo(CO)_2(NO)$ (**2a**) and $HB(3,5\text{-}Me_2Pz)_3W(CO)_2(NO)$ (**3a**) (where $HB(3,5\text{-}Me_2Pz)_3$ = hydridotris(3,5-dimethylpyrazolyl)borate). The corresponding thionitrosyl complexes $HB(3,5\text{-}Me_2Pz)_3Mo(CO)_2(NS)$ (**2b**) and $HB(3,5\text{-}Me_2Pz)_3W(CO)_2(NS)$ (**3b**) have been synthesized according to the method of Hubbard and Lichtenberger.[3]

The UV–vis spectra were measured on an IBM 9420 spectrophotometer in a 1-cm quartz cell; IR spectra were measured on a Perkin-Elmer 983 spectrometer.

NMR spectra were obtained on a WM250 NMR spectrometer. For the ^{14}N NMR (18.1 MHz) a 10-mm broad-band probe (9–36 MHz) was used. Nitromethane (neat) was the external standard. The ^{13}C NMR spectra were measured with a 10-mm broad-band probe (32–105 MHz) at 62.9 MHz, with Me_4Si as internal reference. The ^{95}Mo NMR spectra were measured on a 10-mm molybdenum probe (16.3 MHz), and a 2 M Na_2MoO_4 solution in H_2O at pH 11 was used as an external standard as previously described.[5] All solvents were dried prior to use, and the NMR spectra were measured in sealed NMR tubes under nitrogen or argon at room temperature. Solution concentrations were usually 0.1 M; less soluble complexes were measured as saturated solutions. The NMR data are collected in Table I.

Discussion

In a previous paper[1] we studied several piano stool complexes with the general formula $(T)Mo(CO)_2(NO)$ (where T = $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}Me_5C_5$, $HB(3,5\text{-}Me_2Pz)_3$, $HB(Pz)_3$). The ^{95}Mo NMR spectrum for these complexes is split into a triplet due to spin–spin coupling between ^{95}Mo and ^{14}N. For the $HB(3,5\text{-}Me_2Pz)_3$ complex (**2a**) spin–spin coupling is 44 Hz and is resolved at 423 K in DMF. The corresponding thionitrosyl complex (**2b**) showed no splitting up to 413 K in DMF where the complex decomposed. The ^{14}N resonances of the hydridotris(3,5-dimethylpyrazolyl)borate ligands are very broad (~850 Hz) for all complexes and are essentially indistinguishable from the free ligand (−13 ppm).[1]

Table I. NMR Data

compd	$\delta(^{13}C)^a$ CO	$\delta(^{14}N)^b$ NO	$\delta(^{95}Mo)^c$
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ (**1a**)	239^d	55 (40)	...
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ (**1b**)	237^d	104 (90)	...
$HB(3,5\text{-}Me_2Pz)_3Mo(CO)_2(NO)$ (**2a**)	223	$17\ (130)^e$	$-743\ (60)^e$
$HB(3,5\text{-}Me_2Pz)_3Mo(CO)_2(NS)$ (**2b**)	225	64 (300)	−192 (50)
$HB(3,5\text{-}Me_2Pz)_3W(CO)_2(NO)$ (**3a**)	221	−4 (110)	...
$HB(3,5\text{-}Me_2Pz)_3W(CO)_2(NS)$ (**3b**)	227	23 (300)	

[a] In $CH_2Cl_2/CDCl_3$ relative to Me_4Si. [b] In CH_2Cl_2 relative to nitromethane (neat). [c] In CH_2Cl_2 relative to 2 M Na_2MoO_4 in H_2O at pH 11. [d] Reference 2. [e] Reference 1.

The IR and UV–vis results for the complexes are listed in Table II. The carbonyl stretching frequencies increase only slightly from the nitrosyl to thionitrosyl complexes of chromium and molybdenum. For the pair of tungsten complexes, one CO frequency increases slightly and one decreases slightly when the NO group is replaced by the NS group. As we have discussed elsewhere,[6-8] the loss of back-bonding electron density at the metal when NO is replaced by NS is offset by the lower electronegativity of sulfur in comparison to oxygen, which pushes additional charge toward the nitrogen, and by an increased interaction of the filled NS π orbitals with the filled metal π orbitals. The net result is only a slight perturbation of the electron distribution in the vicinity of the carbonyls. This conclusion is supported by the ^{13}C NMR of the carbonyls (Table I), which show very small (2–6 ppm) shifts of the ^{13}C resonances between the nitrosyl and thionitrosyl complexes. It is also supported by the very small shifts of the ^1H (<0.05 ppm shifts) and ^{13}C (<3 ppm) signals of the hydridotris(3,5-dimethylpyrazolyl)borate[3] and cyclopentadienyl[2] ligands.

The ^{13}C NMR results for the carbonyl ligands are in striking contrast to the ^{14}N NMR data of the coordinated nitrosyl and thionitrosyl groups (Table I). The ^{14}N resonance increases by as much as 49 ppm for an NS complex compared to the analogous NO complex. This deshielding of the nitrogen is accompanied by a doubling of the line width, suggesting a faster spin–spin relaxation time, T_2. For a given set of ligands, the nitrogen chemical shift decreases as the metal center changes from Cr to Mo to W. This latter effect was observed previously in ^{15}N studies of $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ complexes (where M = Cr, Mo, or W) and correlates with the increased back-bonding availability of electrons on the metal center,[9] producing a more shielded nitrogen atom.[10] This trend is also roughly followed by the NX stretching frequencies. On the other hand, the increased chemical shift (deshielding) of the ^{14}N resonance from M–NO to M–NS does not follow the expected increase in electron density at nitrogen that results from the lower electronegativity of the sulfur atom and the increased back-bonding from the metal. This deshielding of the ^{14}N nucleus reflects the dominance of the paramagnetic term in the expression for nuclear resonance shifts.[11] Similar considerations have been used to explain the properties of metal–thiocarbonyl complexes in comparison to metal carbonyls.[12]

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(1) Minelli, M.; Hubbard, J. L.; Christensen, K. A.; Enemark, J. H. *Inorg. Chem.* **1983**, *22*, 2652.

(2) Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3548.

(3) Hubbard, J. L.; Lichtenberger, D. L. *Inorg. Chem.* preceding paper in this issue.

(4) McCleverty, J. A.; Seddon, D.; Bailey, N. A.; Walker, N. W. *J. Chem. Soc., Dalton Trans.* **1976**, 898.

(5) Christensen, K. A.; Miller, P. E.; Minelli, M.; Rockway, T. W.; Enemark, J. H. *Inorg. Chim. Acta* **1981**, *56*, L27.

(6) Hubbard, J. L.; Lichtenberger, D. L. *Inorg. Chem.* **1980**, *19*, 1388.

(7) Hubbard, J. L.; Lichtenberger, D. L. *Inorg. Chem.* **1980**, *19*, 3865.

(8) Hubbard, J. L.; Lichtenberger, D. L., submitted for publication in *Inorg. Chem.*

(9) Hubbard, J. L.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 2132.

(10) Botto, R. E.; Kolthammer, B. W. S.; Legzdins, P.; Roberts, J. D. *Inorg. Chem.* **1979**, *18*, 2049.

(11) Webb, G. A. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; p 49.

0020-1669/84/1323-2721$01.50/0

Table II. IR and UV-Vis Data

compd	IR[a] ν_{CO}, cm^{-1}	IR[a] ν_{NX}, cm^{-1}	UV-vis[b] λ_{max}, nm	UV-vis[b] ϵ, M^{-1} cm^{-1}
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ (1a)	2028[c]	1713[c]	590 (sh)	30
			480 (sh)	120
	1955[c]		355 (sh)	720
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ (1b)	2033[c]	1180[c]	470	310
	1962[c]			
$HB(3,5\text{-}Me_2Pz)_3Mo(CO)_2(NO)$ (**2a**)	1997	1650	480 (sh)	120
	1905		435	200
$HB(3,5\text{-}Me_2Pz)_3Mo(CO)_2(NS)$ (**2b**)	2003	1125	515	200
	1924	1136	445	230
			415 (sh)	210
$HB(3,5\text{-}Me_2Pz)_3W(CO)_2(NO)$ (3a)	1993	1640	480 (sh)	180
	1884		425	320
$HB(3,5\text{-}Me_2Pz)_3W(CO)_2(NS)$ (3b)	1988	1127	510	290
	1902	1140	445	350

[a] KBr pellet. [b] In CH_2Cl_2; sh = shoulder. [c] In hexane; ref 1.

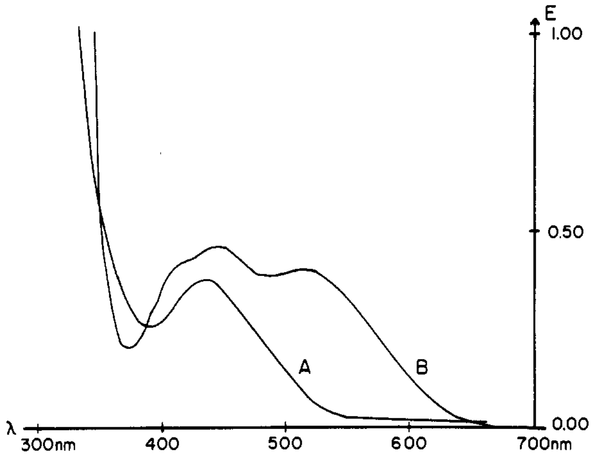

Figure 1. UV-vis spectrum: (A) $HB(3,5\text{-}Me_2Pz)_3Mo(CO)_2(NO)$, 1.90×10^{-3} M in CH_2Cl_2; (B) $HB(3,5\text{-}Me_2Pz)_3Mo(CO)_2(NS)$, 2.0×10^{-3} M in CH_2Cl_2.

The ^{95}Mo NMR results provide unique information in support of a major contribution from the paramagnetic term to the observed chemical shift differences. The ^{95}Mo chemical shift *increases* by more than 550 ppm when NO is replaced by NS. This very large increase is not expected from the relatively small charge distribution changes at the metal, which are indicated by the carbonyl stretching frequencies and the ^{13}C NMR. Equally important, *both* the ^{95}Mo and ^{14}N chemical shifts increase substantially. This deshielding of both nuclei correlates with a decrease in the energies of the low-lying excited states of the complexes as evidenced by the colors of the complexes. The nitrosyl complexes are generally yellow in solution, while the thionitrosyl complexes are more red. The bathochromic shifts of the absorptions in the UV-vis spectra are shown in Figure 1. Photoelectron spectra for the chromium complexes[6,8] also show that the separation between ground and excited states (ΔE) is less for the thionitrosyl complex. In addition, the photoelectron spectra show that the M–NX σ-bonding orbital is more easily ionized in the thionitrosyl complexes. A transition from this orbital to the lowest unoccupied π-type orbital, which is delocalized over the {MNX} triatomic fragment, will contribute to the paramagnetic terms of both the metal and nitrogen resonances. Since ΔE occurs in the denominator of the expression for paramagnetic shielding,[11] the Mo and N atoms in the thionitrosyl complexes will both exhibit larger chemical shifts than in the nitrosyl complexes. It is interesting that the magnitude of the Mo chemical shift change in MoNS complexes is comparable to that for replacement of a terminal oxo group (Mo=O) by a terminal sulfido group (Mo=S) in Mo(VI) complexes.[13,14]

This work shows the value of heteronuclear NMR investigation of metal complexes, which includes NMR of the metal center. It is interesting that the substantial changes in electron distribution and bonding in the M–NX portion of the molecule, as evidenced by the very large changes in the ^{14}N and ^{95}Mo chemical shifts, occur in such a way that the carbonyls experience only a small perturbation, as evidenced by the essentially unshifted ^{13}C resonances. These results provide additional justification for describing such complexes as derivatives of $\{MNX\}^6$ triatomic fragments.[15]

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Registry No. **1a**, 36312-04-6; **1b**, 66539-91-1; **2a**, 86272-24-4; **2b**, 90605-26-8; **3a**, 24899-06-7; **3b**, 90605-27-9; ^{95}Mo, 14392-17-7; N, 7727-37-9.

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(12) Lichtenberger, D. L.; Fenske, R. F. *Inorg. Chem.* **1976**, *15*, 2015.

(13) Lutz, O.; Nolle, A.; Kroneck, P. *Z. Naturforsch., A* **1976**, *31A*, 454; **1977**, *32A*, 505.

(14) (a) Gheller, S. F.; Hambley, T. W.; Traill, P. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Aust. J. Chem.* **1982**, *35*, 2183. (b) Minelli, M.; Enemark, J. H.; Wieghardt, K.; Hahn, M. *Inorg. Chem.* **1983**, *22*, 3952.

(15) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

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^{59}Co NMR of a Cobalt(III) Spin-Crossover Compound

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The cobalt(III) ion has a low-spin electronic configuration in most of its octahedral coordination compounds. Only the fluoride complexes $[CoF_6]^{3-}$ and $[CoF_3(H_2O)_3]$ are known to exist in the high-spin configuration.[2]

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(1) (a) Tel-Aviv University. (b) TH Aachen.

(2) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 775. A few nonoctahedral Co^{III} complexes have been reported that possess a spin-triplet groundstate or close lying excited states. See e.g.: McKenzie, E. D.; Worthington, J. M. *Inorg. Chim. Acta* **1976**, *16*, 9 and references therein.