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### Authors

Finn, Patricia  
Jolly, William L.

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Patricia Finn and William L. Jolly

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Contribution from  
the Department of Chemistry of the University of California and the  
Inorganic Materials Research Division of the Lawrence Berkeley Laboratory,  
Berkeley, California 94720

The Nitrogen 1s Binding Energies of Transition Metal Nitrosyls

By Patricia Finn and William L. Jolly\*

The bonding and electronic structure of transition metal nitrosyls have been frequently studied in recent years.<sup>1-3</sup> Two limiting situations have been identified: linearly coordinated  $\text{NO}^+$  groups and angularly coordinated ("bent")  $\text{NO}^-$  groups. We have investigated the X-ray photoelectron spectra<sup>4</sup> of a series of these compounds to attempt correlations of the nitrogen 1s electron binding energy with structure, electronic features, and N-O stretching frequency.

Experimental Section

The compounds were kindly supplied by Philip G. Douglas and Robert D. Feltham of the University of Arizona, by G. Dolcetti, P. Farnham, and James P. Collman of Stanford University, and, in the case of  $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$ ,<sup>5</sup> by Mark Iannone of this department.

Samples were prepared by brushing the powdered material onto double-faced conducting tape attached to an aluminum plate. The reproducibility was  $\pm 0.2$  eV. In each case the carbon 1s line (arising from pump oil which forms a film on the samples) was recorded and used as a reference peak. Individual lines had widths at half-height of 1.2-2.8 eV; broader lines were due to decomposition or to the presence of a second peak.

The kinetic energy of the photoelectron,  $E_K$ , was measured in an iron-free, double-focusing magnetic spectrometer<sup>6</sup> in which the incident radiation,  $E_{h\nu}$ , was magnesium  $K_{\alpha}$  X-radiation (1253.6 eV) and for which the work function,  $\phi_s$ , was taken as 4.0 eV. The nitrogen 1s binding energy,  $E_B$ , (the difference between the Fermi level and the 1s atomic level energy) was calculated from the relation  $E_B = E_{h\nu} - E_K - \phi_s$ .

### Results and Discussion

The data are presented in Table I. It was found advantageous to categorize the compounds in terms of the metal d electron configurations by making the arbitrary assumption that the nitrosyl groups were  $\text{NO}^+$  ions.

The first six compounds in Table I are six-coordinate and formally have 5 or 6 d electrons. As far as is known, the NO groups in these compounds are linearly coordinated. The nitrogen 1s binding energies of this set of compounds are all within  $\pm 0.6$  eV of 400.1 eV except for the case of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ , for which the binding energy is 403.3. The high value for the latter compound is indicative of a relatively high positive charge on the NO group and may be rationalized by the facts that the compound is the only one in which the metal is not in an abnormally low oxidation state and in which all of the other five ligands are strong  $\pi$  acceptors. It is noteworthy that the N-O stretching frequency for  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  is by far the greatest for this set of compounds - again indicating minimal electron donation into the  $\pi$  orbitals of the  $\text{NO}^+$  group.

Table I

Nitrogen 1s Binding Energies and N-O Stretching Frequencies  
for Transition Metal Complexes

Cpd. No.	Compound	No. of d Electrons <sup>a</sup>	Nitrogen 1s Binding Energy (eV)	Nitrosyl Stretching Frequency (cm <sup>-1</sup> )	Ref.
1	MoCl <sub>2</sub> (NO) <sub>2</sub> (diars)	6	399.6	1760, 1670	b
2	<u>trans</u> -[CrCl(NO)(diars) <sub>2</sub> ]ClO <sub>4</sub>	5	400.7	1690	b
3	<u>trans</u> -[RuCl(NO)(diars) <sub>2</sub> ]Cl <sub>2</sub>	6	400.0	1883	c
4	[(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> P] <sub>3</sub> [Mn(NO)(CN) <sub>5</sub> ]·3H <sub>2</sub> O	6	399.7	1700	d
5	K <sub>3</sub> [Cr(NO)(CN) <sub>5</sub> ]	5	400.7 <sup>e</sup>	1645	f
6	Na <sub>2</sub> [Fe(NO)(CN) <sub>5</sub> ]·2H <sub>2</sub> O	6	403.3	1939	g
7	[π-C <sub>5</sub> H <sub>5</sub> Cr(NO) <sub>2</sub> ] <sub>2</sub>	7	400.7	1672, 1505	h
8	RhI <sub>2</sub> (NO)(P(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ) <sub>2</sub>	8	400.3	1615	i
9	RhCl <sub>2</sub> (NO)(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub>	8	401.5	1630	j
10	CoCl <sub>2</sub> (NO)(diphos)	8	400.7	1665	i
11	<u>trans</u> -[FeCl(NO)(diars) <sub>2</sub> ]ClO <sub>4</sub>	7	400.0	1620	k
12	[Co(NO)(NH <sub>3</sub> ) <sub>5</sub> ]Cl <sub>2</sub>	8	400.7	1620	l
13	<u>trans</u> -[CoCl(NO)(diars) <sub>2</sub> ]Cl	8	400.5	1562, 1548	m
14	[Co(NO)(diars) <sub>2</sub> ][ClO <sub>4</sub> ] <sub>2</sub>	8	402.3	1852	m
15	CoCl <sub>2</sub> (NO)(P(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ) <sub>2</sub>	8	401.7, 399.6	1735, 1630	j
16	CoCl <sub>2</sub> (NO)( $\zeta$ (n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> ) <sub>2</sub>	8	401.5, 399.7	1720, 1650	j
17	[Fe(NO)(diars) <sub>2</sub> ][ClO <sub>4</sub> ] <sub>2</sub>	7	401.2, 399.6	1760	k
18	[RuCl(NO) <sub>2</sub> (P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	8	402.6, 400.2	1850, 1687	j

19	$[\text{Rh}(\text{NO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{PF}_6$	10	401.1	1730,1720	i
20	$[\text{Ir}(\text{NO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{PF}_6$	10	400.2	1760,1700	i
21	$\text{Co}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_3$	10	400.0	1738	n
22	$\text{Co}(\text{NO})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$	10	400.8	1714	n
23	$\text{Rh}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_3$	10	400.8	1650	n
24	$\text{Ir}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_3$	10	400.3	1615	n
25	$\text{Ir}(\text{NO})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$	10	399.6	1645	n
26	$\text{Ru}_3(\text{NO})_2(\text{CO})_{10}$	10	400.4 <sup>o</sup>	1580,1500	i

<sup>a</sup> Based on the assumption of  $\text{NO}^+$  nitrosyl groups.

<sup>b</sup> R. D. Feltham, W. Silverthorn and G. McPherson, Inorg. Chem., **8**, 344 (1969).

<sup>c</sup> P. G. Douglas, R. D. Feltham and H. G. Metzger, J. Amer. Chem. Soc., **93**, 84 (1971).

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<sup>e</sup> Ref. 9.

<sup>f</sup> W. P. Griffith, J. Lewis and G. Wilkinson, J. Chem. Soc., 872 (1959).

<sup>g</sup> G. Paliani, A. Poletti and A. Santucci, J. Mol. Struc., **8**, 63 (1971).

<sup>h</sup> Ref. 8.

<sup>i</sup> Private communication, J. P. Collman.

<sup>j</sup> Ref. 2.

<sup>k</sup> W. Silverthorn and R. D. Feltham, Inorg. Chem., **6**, 1662 (1967).

<sup>l</sup> E. P. Bertin, S. Mizushima, T. J. Lane and J. V. Quagliano, J. Amer. Chem. Soc. **81**, 3821 (1959).

<sup>m</sup> R. D. Feltham and R. S. Nyholm, Inorg. Chem., **4**, 1334 (1965).

<sup>n</sup> Ref. 1.

<sup>o</sup> Very broad because of decomposition.

The second set of compounds in Table I formally have 7 or 8 d electrons and are either five- or six-coordinate.<sup>7</sup> Most of the binding energies lie within  $\pm 0.4$  eV of 400.3 eV; the two exceptions are compounds 9 and 14, with binding energies of 401.5 and 402.3 eV, respectively. It may be significant that both of the latter compounds are five-coordinate; one would expect a lower electron density on the metal and the attached nitrosyl group in a five-coordinate complex than in a six-coordinate complex. However, the low binding energies of the other two five-coordinate complexes, compounds 8 and 10, are then difficult to rationalize. In this set of eight compounds, compound 14 has both the highest binding energy and the highest N-O stretching frequency.

It is interesting that, although compound 7 contains both terminal and bridging NO groups,<sup>8</sup> only one nitrogen 1s peak was observed. Apparently, the NO groups are so similar in electron density that they are indistinguishable by X-ray photoelectron spectroscopy.

A binding energy of 402.0 eV was previously reported<sup>9</sup> for compound 12,  $[\text{Co}(\text{NO})(\text{NH}_3)_5]\text{Cl}_2$ . We repeated this measurement several times with samples that were shown to be pure by magnetic susceptibility measurements, and consistently observed one slightly broadened peak due to the  $\text{NH}_3$  groups (at 400.2 eV) and the NO group. By computer fitting, we were unable to ascertain the position of the NO peak more precisely than  $400.7 \pm 1.3$  eV.

It should be noted that, on going from compound 13 to compound 14, the complex ion changes only by the removal of a chloride ion - with the consequent change in coordination number from six to five. The



increase in binding energy of 1.8 eV and the increase in the N-O stretching frequency of  $300 \text{ cm}^{-1}$  are the expected consequences of reduced electron donation into the  $\text{NO}^+$   $\pi$  orbitals.

The third set of compounds in Table I formally have 7 or 8 d electrons and show two separate nitrogen 1s peaks. For each of the cobalt compounds 15 and 16, two different coordination geometries are thought to be present:<sup>2</sup> a trigonal bipyramidal structure with an equatorial linear nitrosyl and a square pyramidal structure with an apical bent nitrosyl. The two nitrogen 1s binding energies observed for both of these compounds are separated by about 2 eV. Presumably the bent nitrosyl corresponds to the lower binding energy and the linear nitrosyl corresponds to the higher binding energy in each case.

Two nitrogen 1s binding energies were observed for compound 17,  $[\text{Fe}(\text{NO})(\text{diars})_2](\text{ClO}_4)_2$ , although only one N-O stretching frequency has been reported. Perhaps different structural forms are present, as postulated for compounds 15 and 16. This iron compound can be compared to its six-coordinate analog - compound 11, trans- $[\text{FeCl}(\text{NO})(\text{diars})_2]\text{ClO}_4$ . The binding energy increases 1.2 eV and the stretching frequency increases  $140 \text{ cm}^{-1}$  on changing from the six- to the five-coordinate system, smaller changes than observed for the analogous cobalt system.

In the ruthenium complex, compound 18, two different types of nitrosyl group are bonded to the same metal atom.<sup>3</sup> This square pyramidal compound has an apical bent nitrosyl and a linear equatorial nitrosyl. Presumably, the higher binding energy (402.6 eV) and higher N-O frequency ( $1850 \text{ cm}^{-1}$ ) correspond to the linear nitrosyl, and the lower binding

energy (400.2 eV) and lower N-O frequency ( $1687 \text{ cm}^{-1}$ ) correspond to the bent nitrosyl.

The fourth set of compounds in Table I (compounds 19-26) formally have ten d electrons and, except for compound 26, are four-coordinate. Probably because of the high electron densities on the metal atoms, the binding energies are low. The low N-O stretching frequencies are consistent with these results.

We draw the overall conclusion that there is a definite correlation between the nitrogen 1s binding energy of a nitrosyl group and the electron density on that group. Bent nitrosyls have low binding energies. Linear nitrosyls can have either low or high binding energies, depending on the extent of  $\pi$  back-bonding from the metal atom. The binding energies are at least roughly correlated with the N-O stretching frequencies: when one is high or low, so is the other.

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