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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.[1-6] Two limiting situations have been identified: linearly coordinated NO^+ groups and angularly coordinated ("bent") NO^- groups. We have investigated the X-ray photoelectron spectra[7] of a series of these compounds to attempt correlations of the nitrogen 1s electron binding energy with structure,[8-19] electronic features, and N-O stretching frequency.[16,20-39]

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 $[Co(NH_3)_5NO]Cl_2$,[40] by Mark Iannone of this department.

The powdered samples were brushed onto double-faced conducting tape attached to an aluminum plate. The reproducibility was ± 0.2 eV. In each case the carbon 1s line (due to a film of pump oil 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[41] in which the incident radiation, $E_{h\nu}$, was magnesium K_α X-radiation (1253.6 eV) and for which the work function, ϕ_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 NO^+ ions. (Although this assumption is illogical for the few compounds that contain "bent" NO groups, we made the assumption to simplify the classification of the compounds.)

The first seven compounds in Table I are six-coordinate and formally have 5 or 6 d electrons. In compounds 1-4, the metal atoms are in "abnormally low" oxidation states (0, +1, and +1 for Mo, Cr, and Mn, respectively), whereas in compounds 5-7, the metal atoms are in "normal" oxidation states (+2 for Ru and Fe). As far as is known, the NO groups in these seven compounds are essentially linearly coordinated. The nitrogen 1s binding energies are all within ± 0.6 eV of 400.1 eV except for compounds 6 and 7, for which the binding energies are 402.9[42] and 403.3 eV, respectively. The high values for the latter compounds are indicative of relatively high positive charges on the NO groups and may be rationalized by the fact that in these compounds the metal atoms are

Table I

Nitrogen 1s Binding Energies, N-O Stretching Frequencies, and M-N-O Bond Angles for some Transition Metal Complexes

Compound Number	Compound	No. of d electrons[a]	Nitrogen 1s Binding Energy (eV)	Nitrosyl Stretching Frequency (cm^{-1})	Ref.	M-N-O angle (°)	Ref.
1	$MoCl_2(NO)_2$(diars)	6	399.6	1760, 1670	20		
2	trans-$[CrCl(NO)(diars)_2]ClO_4$	5	400.7	1690	20		
3	$K_3[Cr(NO)(CN)_5]$	5	400.7[b]	1645	21	176.0[c]	8
4	$[(C_6H_5)_4P]_3[Mn(NO)(CN)_5]\cdot 3H_2O$	6	399.7	1725[d]	22	174.3[d]	9
5	trans-$[RuCl(NO)(diars)_2]Cl_2$	6	400.0	1883	23		
6	trans-$[FeCl(NO)(diars)_2](ClO_4)_2$	6	402.9[e]	1865	24		
7	$Na_2[Fe(NO)(CN)_5]\cdot 2H_2O$	6	403.3	1939	25	178.3	10
8	$[\pi\text{-}C_5H_5Cr(NO)_2]_2$	7	400.7	1672, 1505	26		
9	$RhI_2(NO)[P(CH_3)(C_6H_5)_2]_2$	8	400.3	1628[f]	27	120[g]	11
10	$RhCl_2(NO)[P(C_6H_5)_3]_2$	8	401.5	1630	28	123[h]	12
11	$CoCl_2(NO)$(diphos)	8	400.7	1676	29		
12	trans-$[FeCl(NO)(diars)_2]ClO_4$	7	400.0	1620	30		
13	$[Co(NO)(NH_3)_5]Cl_2$	8	400.7	1620	31	119.0	13
14	trans-$[CoCl(NO)(diars)_2]Cl$	8	400.5	1562, 1548	32	124.4[i]	14
15	$[Co(NO)(diars)_2](ClO_4)_2$	8	402.3	1852	32	174[j]	15

(Table cont'd next pg.)

16	$CoCl_2(NO)[P(CH_3)(C_6H_5)_2]_2$	8	401.7, 399.6	1735, 1630	28		
17	$CoCl_2(NO)[P(n\text{-}C_4H_9)_3]_2$	8	401.5, 399.7	1720, 1650	28		
18	$[Fe(NO)(diars)_2](ClO_4)_2$	7	401.2, 399.6	1760	30		
19	$\{RuCl(NO)_2[P(C_6H_5)_3]_2\}PF_6$	8	402.6, 400.2	1845, 1687	16	179.5, 136.0	16
20	$\{Rh(NO)_2[P(C_6H_5)_3]_2\}PF_6$	10	401.1	1730, 1720	33		
21	$\{Ir(NO)_2[P(C_6H_5)_3]_2\}PF_6$	10	400.2	1760-1715	34	163.5	17
22	$Co(NO)[P(C_6H_5)_3]_3$	10	400.0	1738	35		
23	$Co(NO)(CO)[P(C_6H_5)_3]_2$	10	400.8	1714	35		
24	$Rh(NO)[P(C_6H_5)_3]_3$	10	400.8	1650	36		
25	$Ir(NO)[P(C_6H_5)_3]_2$	10	400.3	1615	37	180	18
26	$Ir(NO)(CO)[P(C_6H_5)_3]_2$	10	399.6	1645	37		
27	$Ru_3(NO)_2(CO)_{10}$	10	400.4[k]	1524, 1508	38		
28	$NiCl(NO)[P(C_6H_5)_3]_2$	10	399.8	1735[ℓ]	39		
29	$Ni(N_3)(NO)[P(C_6H_5)_3]_2$	10	399.6	—		152.7	19

[a] Based on the arbitrary assumption of NO^+ nitrosyl groups.

[b] Reference 44.

[c] The bond angle refers to the corresponding $Co(en)_3^{3+}$

[d] Both the stretching frequency and bond angle are for the corresponding potassium salt.

[e] Reference 42.

[f] The stretching frequency is for the compound containing the triphenylphosphine ligand.

[g] The bond angle refers to the analogous iridium complex in which one CH_3 group has been replaced by an I atom.

[h] The bond angle refers to the analogous iridium complex.

[i] The bond angle refers to the analogous compound in which ethylenediamine groups have replaced the diarsine groups.

[j] The bond angle refers to the analogous ruthenium complex in which two diphosphine groups have replaced the diarsine groups.

[k] Very broad signal because of decomposition.

[ℓ] The stretching frequency is for the analogous bromo and iodo compounds.

in a "normal" oxidation state. It is noteworthy that the N-O stretching frequencies for compounds 6 and 7 are very high - a further indication of minimal electron donation into the π orbitals of the NO^+ groups. It is difficult to explain the low binding energy observed for compound 5, which contains ruthenium in a "normal" oxidation state and for which the N-O stretching frequency is very high. Perhaps the recorded binding energy corresponds to a decomposition product.[42]

The second set of compounds in Table I formally have 7 or 8 d electrons and are either five- or six-coordinate.[43] Most of the binding energies lie within ± 0.4 eV of 400.3 eV; the two exceptions are compounds 10 and 15, 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 9 and 11, are then difficult to rationalize. In this set of eight compounds, compound 15 has both the highest binding energy and the highest N-O stretching frequency.

It is interesting that, although compound 8 contains both terminal and bridging NO groups,[26] 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[44] for compound 13, $[Co(NO)(NH_3)_5]Cl_2$. 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 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 ± 1.3 eV.

It should be noted that, on going from compound 14 to compound 15, 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 cm^{-1} are the expected consequences of reduced electron donation into the NO^+ π 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 16 and 17, two different coordination geometries are thought to be present:[28] 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 18, $[Fe(NO)(diars)_2](ClO_4)_2$, although only one N-O stretching frequency has been reported. Three possible explanations come to mind. Perhaps different structural forms are present (as postulated for compounds 16 and 17), and the N-O stretching frequency of one form is of low intensity. Perhaps the spectral splitting is due to the paramagnetism of the sample.

Finally, it is not unlikely that the sample underwent decomposition in the X-ray beam and that the two peaks are due to the compound and its decomposition product.[45]

In the ruthenium complex, compound 19, two different types of nitrosyl group are bonded to the same metal atom.[16] 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 (1845 cm^{-1}) correspond to the linear nitrosyl, and the lower binding energy (400.2 eV) and lower N-O frequency (1687 cm^{-1}) correspond to the bent nitrosyl.

The fourth set of compounds in Table I (compounds 20-29) formally have ten d electrons and, except for compound 27, 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 π 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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