TABLE I
EXPERIMENTAL INTENSITY RATIOS, J, AT 25°

10^3c, g/ml	J
$MgA_2 \cdot 2H_2O$ in CH_3OH	
0	0.25
2.75	0.38
7.15	0.53
10.90	0.62
13.36	0.70
25.06	1.09
MgA_2 in CH_2Cl_2	
0	0.71
2.47	3.06
2.90	3.29

10^3c, g/ml	J
$MgA_2 \cdot 2H_2O$ in DMF	
0	0.38
2.39	0.41
5.76	0.45
9.55	0.50
15.27	0.58
25.17	0.72
36.64	0.88
$NiA_2 \cdot 2H_2O$ in CH_3OH	
0	0.25
3.88	0.43
5.60	0.48
8.40	0.57
16.80	0.85

10^3c, g/ml	J
$C_{10}H_8$ in DMF	
0	0.38
53.12	1.24
58.87	1.31
68.94	1.45
80.20	1.62
94.75	1.87
NiA_2 in CCl_4	
0	0.74
3.80	0.84
7.60	0.91
11.40	1.06
15.82	1.22
24.07	1.52

by-product. The white, solid product was recrystallized several times from methanol. Pumping on the product in a vacuum oven at 100° through a cold trap followed by gas chromatographic analysis of the condensate confirmed that it was hydrated rather than methylated. *Anal.* Calcd: H_2O, 13.9. Found: H_2O, 14.3.

Magnesium Acetylacetonate, $Mg(C_5H_7O_2)_2$.—The dihydrate was heated *in vacuo* at 100° for 12 hr. *Anal.* Calcd: Mg, 10.9; C, 54.0; H, 6.3. Found: Mg, 10.8; C, 5319; H, 6.4.

Results and Discussion

The evaluation of the solvent parameters is summarized in Table II; the results are given in Table III.

TABLE II
SOLVENT PARAMETERS AT 25°

	J_0	γ	C_p, cal/ml deg[a]	$10^4 \partial n/\partial T$	S, mol/ml
Methanol	0.25	1.205[b]	0.4760[c]	−3.90[d]	3.75
Methylene chloride	0.71	1.521[e]	0.3748[e]	−6.0[f]	3.43
Carbon tetrachloride	0.74	1.440[b]	0.3243[g]	−5.74[d]	2.95
Dimethylformamide					4.42[h]

[a] Densities for converting to these units came from the reference in footnote *f*. [b] E. B. Freyer, J. C. Hubbard, and D. H. Andrews, *J. Amer. Chem. Soc.*, **51,** 759 (1929). [c] H. G. Carlson and E. F. Westrum, Jr., *J. Chem. Phys.*, **54,** 1464 (1971). [d] Measured in this laboratory at 6328 Å. [e] J. L. Hunter and H. D. Dardy, *J. Chem. Phys.*, **42,** 2961 (1965). [f] "Selected Values of Properties of Chemical Compounds," Manufacturing Chemists Association Research Project, Thermodynamics Research Center, Texas A & M University, College Station, Texas. [g] J. F. G. Hicks, J. G. Hooley, and C. C. Stephenson, *J. Amer. Chem. Soc.*, **66,** 1064 (1944). [h] Determined experimentally using naphthalene: $\partial n/\partial c = 0.166$, $J - J_0 = 15.6c$, $M = 128.17$.

TABLE III
SOLUTION PARAMETERS AND WEIGHT-AVERAGE MOLECULAR WEIGHTS AT 25°

Complex[a]	Formula wt	Solvent	$\partial n/\partial c$	dJ/dc[b]	M
$MgA_2 \cdot 2H_2O$	258.6	CH_3OH	0.190	32.6	241
$MgA_2 \cdot 2H_2O$	258.6	DMF	0.104	13.7	287
MgA_2	222.5	CH_2Cl_2	0.0966	911	28,500
$NiA_2 \cdot 2H_2O$	293.0	CH_3OH	0.182	34.8	280
NiA_2	256.9	CCl_4	0.0708	32.8	2,220

[a] A = acetylacetonate ligand ($C_5H_7O_2$). [b] From a linear least-squares fit to the data in Table I.

The hydrates, which are monomeric as expected, bind their water strongly and may be recrystallized unchanged from the coordinating solvents in which they were studied. Not surprisingly, we found the molecular weight of MgA_2 in CH_2Cl_2 to be quite sensitive to traces of water. The solubility of water in CH_2Cl_2[3] is such that, at the highest concentration of MgA_2, there would be enough water to hydrate 39% of the MgA_2 if the solvent were previously saturated with water. We removed traces of water by dissolving MgA_2 in hot CH_2Cl_2 and cooling to 0° to precipitate essentially all the complex. Because of the much lower solubility of water in CCl_4,[3] we did not attempt to dry this solvent.

Our results for NiA_2 are not necessarily incompatible with earlier ebullioscopic results in CCl_4,[4] which yielded a number-average molecular weight equivalent to that of the trimer, but only point to a broad distribution of oligomers. This situation has been already suggested for the analogous cobalt complex, CoA_2.[5] As a simple example of the effect of a broad distribution, equal-weight fractions of $(NiA_2)_2$ and $(NiA_2)_{14}$ would yield a number-average molecular weight of 900 and a weight-average value of 2056.

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Nitrogen 1s Binding Energies of Some Azide, Dinitrogen, and Nitride Complexes of Transition Metals

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We have used X-ray photoelectron spectroscopy to determine the nitrogen 1s binding energies of azide, dinitrogen, and nitride complexes of several transition metals. Such data are of interest because the binding energy shifts can be interpreted in terms of the interaction of the ligands with the transition metal atoms.

Experimental Section

The compounds $Ni(N_3)(NO)[P(C_6H_5)_3]_2$,[1] *trans*-$[Ru(N_3)Cl(diars)_2]$,[2] *trans*-$[Co(N_3)_2(diars)_2]ClO_4$,[2] *trans*-$[Ru(N_2)Cl(diars)_2]$,[2] and $[C_6H_5(N_2)]BF_4$[3] were kindly supplied by Philip G. Douglas and Robert D. Feltham of the University of Arizona. We prepared $\{Cu(N_3)[P(C_6H_5)_3]_2\}_2$,[4] $[Rh(N_3)(CO)_2]_2$,[5] $[As(C_6H_5)_4]_2[Fe(N_3)_5]$,[6] $K_3[Ru_2N(Cl)_8(H_2O)_2]$,[7] and $ReN(Cl)_2[P(C_6H_5)_3]_2$[8] by known procedures. The KBr-pellet infrared spectra of these complexes were in good agreement with the literature data.

The powdered samples were brushed onto double-faced conducting tape attached to an aluminum plate. 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 of 1.4–2.6 eV. The kinetic energy of the photoelectron, E_K, was measured in an iron-free double-focusing magnetic spectrometer[9] in which the incident radiation, $E_{h\nu}$, was magnesium $K\alpha$ 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 energy and the 1s atomic energy), was calculated from the relation $E_B = E_{h\nu} - E_K - \phi_s$.

Results

The data are presented in Table I.

TABLE I

THE NITROGEN 1s BINDING ENERGIES OF SOME TRANSITION METAL COMPLEXES

Compound	Nitrogen 1s binding energy, eV	Intensity ratio	Separation, eV
NaN_3	403.7, 399.3[a]	1:2	4.4
$Ni(N_3)(NO)[P(C_6H_5)_2]_2$	403.8, 399.6	1:2	4.2
trans-$[Ru(N_3)Cl(diars)_2]$	403.9, 399.2	1:2	4.7
trans-$[Co(N_3)_2(diars)_2]ClO_4$	403.2, 399.1	1:2	4.1
$\{Cu(N_3)[P(C_6H_5)_3]_2\}_2$	403.7, 399.2	1:2	4.5
$[Rh(N_3)(CO)_2]_2$	403.2, 399.3	1:2	3.9
$[As(C_6H_5)_4]_2[Fe(N_3)_5]$	402.8, 398.7	1:2	4.1
trans-$[Ru(N_2)Cl(diars)_2]$	402.3, 400.7	1:1	1.6
$Re(N_2)Cl(diphos)_2$	399.9, 397.9[b]	1:1	2.0
$[C_6H_5(N_2)]BF_4$	405.1, 403.8	1:1	1.3
$K_3[Ru_2N(Cl)_8(H_2O)_2]$	399.8		
$ReN(Cl)_2[P(C_6H_5)_3]_2$	398.8		

[a] D. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969). [b] See G. J. Leigh, J. N. Murrell, W. Bremser, and W. G. Proctor, *J. Chem. Soc. D*, 1661 (1970).

Azide Complexes.—The first group of compounds in Table I contain azide ions in various environments. It is noteworthy that sodium azide and the azide complexes have very similar spectra, with two peaks separated by 4.3 ± 0.4 eV. The peak at lower binding energy (corresponding to the two end atoms) has twice the intensity of the other peak (corresponding to the middle atom). These results indicate that the internal bonding of the azide ion is essentially unaffected by coordination to a transition metal atom; that is, the azide ion appears to be linked to the metal atom by an ionic bond with little polarization. The infrared spectra and X-ray diffraction structural data of such compounds are consistent with these conclusions. Thus the asymmetric stretching frequency and the bending frequency of the azide ion in complexes are almost unchanged from those of the azide ion in sodium azide.[1,2,4–6] The N–N bond distances in azide complexes are within 0.02 Å of that in sodium azide.[10–12]

Both peaks of $[As(C_6H_5)_4]_2[Fe(N_3)_5]$, the only anionic azide complex considered, are appreciably shifted to lower binding energies (by 0.6 and 0.9 eV) from the peaks of sodium azide. Probably the 2− charge on the anion is responsible for the lower binding energies.

Dinitrogen Complexes.—The Ru–N bond length of 1.894 Å for the N_2 group in $[Ru(N_3)(N_2)(en)_2]$[13] is significantly shorter than the Ru–N single-bond distance of 2.144 Å in $[Ru(NH_3)_6]I_2$.[14] Similar evidence for partial multiple-bond character in metal–N_2 bonds is found for other transition metal complexes.[15–18] Thus a dinitrogen complex can be considered to be a hybrid of two major resonance forms, $M{-}N^{+}{\equiv}N$ and $M{=}N^{+}{=}N^{-}$. Because the nitrogen atom directly attached to the metal atom has a formal positive charge in both forms, we expect decreased electron density on this nitrogen atom and a correspondingly higher binding energy. The nitrogen 1s spectrum of *trans*-$[Ru(N_2)Cl(diars)_2]$ consists of two peaks; we assign the higher binding energy to the nitrogen atom directly attached to the ruthenium atom. Leigh, *et al.*,[19] made a similar assignment for $[Re(N_2)Cl(diphos)_2]$.

We found two nitrogen 1s peaks for $[C_6H_5(N_2)]BF_4$, with a peak separation of the same order of magnitude (1.3 eV) as found for the transition metal compounds. However, both peaks are at higher binding energy probably because of the 1+ charge of the diazonium ion. For all resonance forms the nitrogen atom directly attached to the phenyl group has a formal positive charge; therefore the higher binding energy peak is assigned to this nitrogen atom.

Nitride Complexes.—The nitrogen 1s binding energies of $K_3[Ru_2N(Cl)_8(H_2O)_2]$ and $ReN(Cl)_2[P(C_6H_5)_3]_2$ are of interest because these complexes contain nitride ion ligands which are bridging and nonbridging, respectively. In the former complex, two metal atoms compete for the electron density of the bridging nitride; therefore a higher binding energy is observed for this compound even though the complex has a 3− charge.

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