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Electronic Spectra of Zerovalent Hexakis(dinitrogen) and Hexacarbonyl Derivatives of Titanium, Vanadium, and Chromium

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The crystal field and charge-transfer spectra of the title compounds in the visible and near-ultraviolet regions have been analyzed and assigned. Charge transfer from the metal to the ligand, dinitrogen or carbonyl, is observed, with the former to lower energy. The energies of these MLCT bands are discussed in terms of the nature of the M–N$_2$ and M–CO bonds. It is shown that the lower the first-order energy of the acceptor orbital on the ligand, and the better its overlap, the greater is the degree of back-donation in the ground state and the higher is the energy of the charge-transfer excited state. The Dq value for N$_2$ is lower than that for CO and, in these complexes, shows much less sensitivity to the metal.

Since the initial discovery of a dinitrogen–metal complex by Allen and Senoff[2] there has been keen interest in understanding the nature of the metal–dinitrogen bond as a means of permitting the design of complexes capable of fixing and utilizing molecular nitrogen. Since dinitrogen and carbon monoxide are isoelectronic, most authors have made comparisons between these two ligands. Initial controversies based on infrared[3,4] and Mössbauer data[5] have now been resolved with the conclusion that, in comparable environments, the carbonyl group is certainly a better π acceptor than dinitrogen. The early suspicion[6] that this arises as a consequence of the LUMO (π^*) orbital in N$_2$ being appreciably higher in energy than the LUMO orbital in CO appears unfounded. These orbitals are now believed to have comparable energies.[7-9] The lowest energy spin-allowed transition in the free ligands[10,11] (8.33 eV for N$_2$ and 7.98 eV for CO) together with the observation that the HOMO orbitals also have comparable energies[7-9,12] provide support for this conclusion. To throw light on this particular aspect of the problem Fenske and co-workers[12] completed a molecular orbital calculation of Cr(CO)$_6$ and, at that time hypothetical, Cr(N$_2$)$_6$. They concluded that better π-acceptor properties of the carbonyl arose primarily from differences in the off-diagonal elements connecting the metal d orbitals and the π-antibonding orbitals on the ligands. They also noted that N$_2$ was a weaker σ donor than CO as indicated by the smaller degree of σ-electron donation to the metal.

Most recently Ozin and co-workers[13] have studied the infrared spectra of the series of matrix-isolated derivatives Ni(CO)$_m$(N$_2$)$_{4-m}$ which provide convincing evidence that CO is indeed a better π acceptor than N$_2$. Similar conclusions may be drawn from consideration of the ν(NN) stretching frequencies in the pair of complexes[14] [(C$_5$Me$_5$)$_2$Zr(N$_2$)]$_2$(N$_2$) and [(C$_5$Me$_5$)$_2$Zr(CO)]$_2$(N$_2$) and the photoelectron spectra[9] of the pair CpMn(CO)$_3$ and CpMn(CO)$_2$N$_2$.

We analyze here the charge-transfer and d–d spectra of the series MX$_6$, where M = Ti(0), V(0), or Cr(0) and X = N$_2$ or CO, in terms of the above understanding.

The title compounds have been prepared in frozen matrices at liquid helium temperatures by DeVore[15] and by Ozin and co-workers.[16] The UV–visible spectrum of the purported Cr(N$_2$)$_6$ molecule reported by DeVore[15] has been shown[17] by chromium concentration studies to contain absorptions associated with Cr$_x$(N$_2$)$_y$ cluster compounds. We therefore discuss the spectra reported by Ozin and co-workers.[16] These electronic spectra, exhibiting both d–d and charge-transfer bands, are illustrated in Figures 1–4.

The spectra, in general, exhibit relatively weak bands lying at low energies and much stronger bands lying at high energies. In most cases, the weak, low-energy bands can be unequivocally assigned to crystal field d–d transitions, similarly the higher energy more intense peaks are undoubtedly charge-

transfer transitions. These two types of transitions will be dealt with separately.

Crystal Field Transitions

All of the complexes have been studied under concentrated deposition conditions and we are confident that the lowest energy d–d transition has in fact been observed.

We are dealing here with low-spin d^4, d^5, and d^6 species. Although the electronic spectra of low-spin d^6 species are fairly well understood,[18] few low-spin d^4 and d^5 species have been unequivocally assigned, because there exist for these species a relatively large number of spin-allowed electronic states which tend to cluster together in energy. For example, for low-spin d^4 complexes, there are eight transitions with an overall spread of approximately 18B (assuming $C = 4B$), involving 1-e excitation from the t$_{2g}$ to the e$_g$ level. Similarly for d^5 there are eight spin-allowed transitions with an overall spread, in this case of some 31B involving a 1-e excitation to the e$_g$ level.

However, we are primarily interested in obtaining an estimate of the magnitude of 10Dq in these complexes. This information can be obtained with some degree of accuracy by noting the following. (i) The value of the Racah parameter in these zerovalent complexes (Table I) is relatively small and will be further reduced by electron delocalization. The interelectronic repulsion energy in these complexes is likely to be quite small. (ii) Both carbon monoxide and to a lesser degree dinitrogen are strong field ligands. It is therefore reasonable to discuss these complexes in the strong-field approximation. In view of comment (i) the errors introduced by neglecting configurational interaction can be expected to be small.

The observed d–d and charge-transfer energies are listed in Table II. In Table I, we cite the first-order, strong-field energies of the lowest spin-allowed transition. By assuming that the lowest observed electronic band corresponds to this transition and by taking the free-ion B and C values for the zerovalent metal (Table I) and reducing them by some 25%,[18] we can calculate the magnitude of 10Dq in these complexes. The results are shown in Table III.

Note that there is evidence for tetragonal distortion in V(CO)$_6$ from electron spin resonance[19] measurements at liquid helium temperature; moreover, there is a small splitting in the T$_2$ CO and NN stretching frequencies of V(CO)$_6$ and V(N$_2$)$_6$ indicating a correspondingly small distortion or matrix site effect (see ref 16). However, we note at this time that should such tetragonal distortion be present, the 10Dq values for the vanadium derivatives may be underestimated but probably by not more than about 1000 cm^{-1}.

Nothing can be said at this time concerning the assignment of the high-energy d–d transitions in the titanium and vanadium compounds.

Table I. Spectroscopic Data for d^4–d^6 Species

Confign	Ground state	Strong-field energy of 1st spin-allowed d–d transition (low spin)	1st ionization potential, eV	Free-ion M(0) Racah parameters (B, C), cm^{-1}	ΔSPE^a
d^4	$^3T_{1g}$	$10Dq + 2B - C$ (^3E_g)	6.82	560, 1840	$-2D$
d^5	$^2T_{2g}$	$10Dq - 3B - C$ ($^2A_{2g}$)	6.74	578, 2273	$-(4/3)D$
d^6	$^1A_{1g}$	$10Dq - C$ ($^1T_{1g}$)	6.76	790, 2520	$-(2/3)D$

^{a} Change in mean spin-pairing energy for the charge-transfer transition $d^n \rightarrow d^{n-1}\pi^* D \simeq 7B$.
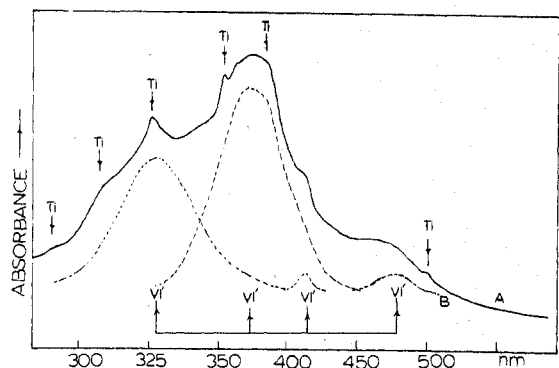

Figure 1. UV–visible spectrum of Ti(N$_2$)$_6$ in N$_2$ formed from Ti/N$_2$ cocondensation at 15 K. VI' refers to the absorptions of Ti(N$_2$)$_6$ whereas the arrows refer to Ti atomic resonance absorptions (see ref 16).
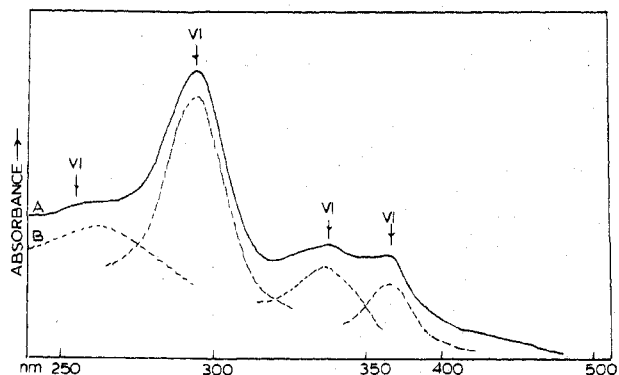

Figure 2. UV–visible spectrum of Ti(CO)$_6$ in CO formed from Ti/CO cocondensation at 10 K. VI refers to the absorption of Ti(CO)$_6$.
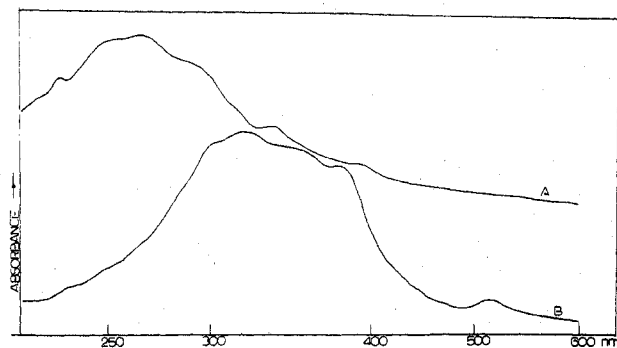
Figure 3. Optical spectrum of (A) V(CO)$_6$ in CO and (B) V(N$_2$)$_6$ in N$_2$ formed from V/CO and V/N$_2$ cocondensation reactions at 10 and 20 K, respectively.

In the Cr(N$_2$)$_6$ compound, there are two low-energy bands observed fairly close together, indeed too close together to be assigned to the first two spin-allowed d–d transitions in a low-spin d^6 complex. Such assignment leads to an unacceptably low value for B. The second band (at 23474 cm^{-1}) is weak and is probably a spin-forbidden transition. The next transition, at 27397 cm^{-1}, for reasons discussed below we prefer to assign to a charge-transfer transition.

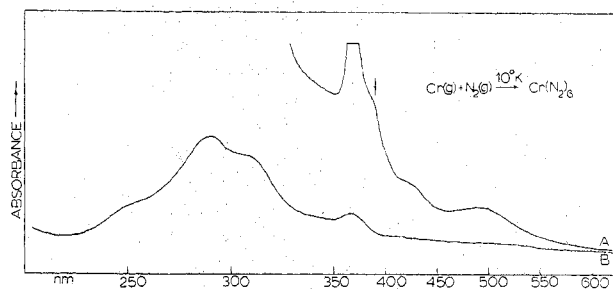**Figure 4.** UV–visible spectrum of Cr(N$_2$)$_6$ in N$_2$ formed from Cr/N$_2$ cocondensation reactions at 15 K. Curve A has a longer deposition time than B. The arrow indicates a Cr$_x$(N$_2$)$_y$ cluster absorption.

Table II. Crystal Field and Charge-Transfer Transition Energies

	M = Ti	M = V	M = Cr	
		M(N$_2$)$_6$		
d–d	20 833	19 455	20 576	
	24 096	23 585	23 474	
Charge transfer	26 738	26 740 ⎫ 29 155 ⎬	27 397	$t_{2g} \rightarrow t_{1u}$ CT1(N$_2$)
	30 581	31 646 ⎫ 33 557 ⎬	32 680 34 602	$t_{2g} \rightarrow t_{2u}$ CT2(N$_2$)
		35 461	40 000	$t_{2g} \rightarrow t_{2g}^*$ (?)
		M(CO)$_6$		
d–d	27 174	25 840	31 350^a	
	29 762	30 478		
Charge transfer		32 154 ⎫		
	33 898	33 784 ⎬ 37 453 ⎭	35 780^a	$t_{2g} \rightarrow t_{1u}$ CT1(CO)
	38 023	40 650 ⎫ 44 248 ⎬	44 480^a	$t_{2g} \rightarrow t_{2u}$ CT2(CO)
			51 280^a	$t_{2g} \rightarrow t_{2g}^*$

^{a} H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, 85, 2922 (1963).

Table III. Estimated 10Dq Values (cm^{-1})^a

Metal	M(N$_2$)$_6$	M(CO)$_6$
Ti	21 370	28 255
V	22 460	28 845
Cr	22 465	33 240

^{a} Calculated from lowest experimental d–d band using the Racah parameters in Table I diminished by 25%.

Charge-Transfer Spectra

The charge-transfer spectra of low-spin d^6 hexacarbonyls and hexacyanides have been discussed in detail by Gray and Beach.[20] We anticipate that the isoelectronic hexakis(dinitrogen) complexes will behave in substantially the same manner. The molecular orbital diagram in Figure 5, based on that for the carbonyls,[20] illustrates the anticipated one-electron energy level order in these complexes. The low-energy charge-transfer transitions arise as a consequence of electronic excitation from the filled or partly filled t_{2g} orbitals on the metal to the low-lying antibonding levels on the ligand of t_{1u} and t_{2u} symmetry. One-electron excitation to these two π^* levels on the ligand gives rise to a number of charge-transfer excited states, shown in Table IV; however some of the
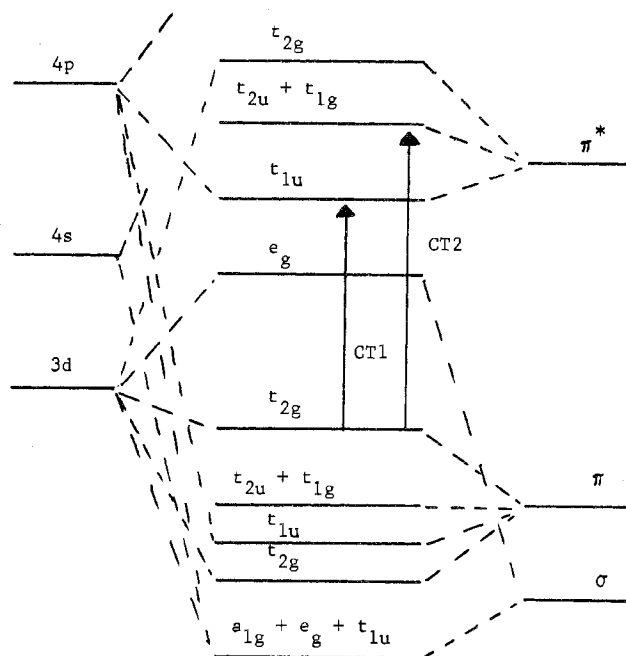
Figure 5. Partial molecular orbital diagram for ML_6 (L = CO, N_2) complexes of a 3d transition metal. The relevant one-electron metal to ligand charge-transfer transitions are illustrated. Diagram is not to scale.

Table IV. Symmetry Species of Possible Spin-Allowed Charge-Transfer States for the Transitions $t_{2g} \to t_{1u}$ and $t_{2g} \to t_{2u}$ in d^4, d^5, and d^6 Low-Spin Octahedral Complexes

	d^4 ($^3T_{1g}$)		d^5 ($^2T_{2g}$)		d^6 ($^1A_{1g}$)	
	Allowed	Forbidden	Allowed	Forbidden	Allowed	Forbidden
$t_{2g} \to t_{1u}$	$4\,^3T_{2u}$ $3\,^3T_{1u}$ $2\,^3E_u$ $^3A_{1u}$	$^3A_{2u}$	$3\,^2T_{2u}$ $4\,^2T_{1u}$ $2\,^2E_u$ $^2A_{2u}$	$^2A_{1u}$	$^1T_{1u}$	$^1T_{2u}$
$t_{2g} \to t_{2u}$	$3\,^3T_{2u}$ $4\,^3T_{1u}$ $2\,^3E_u$ $^3A_{1u}$	$^3A_{2u}$	$4\,^2T_{2u}$ $3\,^2T_{1u}$ $2\,^2E_u$ $^2A_{2u}$	$^2A_{1u}$	$^1T_{1u}$	$^1T_{2u}$

Table V. Band Energy Ratios and Differences

	Ti	V	Cr
$CT1(CO)/CT1(N_2)$	1.26	1.23	1.30
$CT2(CO)/CT2(N_2)$	1.24	1.30	1.28
$CT2(N_2) - CT1(N_2)$,[a] cm^{-1}	3843	4654	6359
$CT2(CO) - CT1(CO)$,[a] cm^{-1}	4125	7985	8700

[a] Mean band energies used where multiple bands occur.

transitions from the ground state to these various excited states are orbitally forbidden. For a d^6 complex, having a $^1A_{1g}$ ground state, only transitions to the $^1T_{1u}$ excited state are allowed.[18,20] There are two such excited states, one arising from excitation to each of the two ligand π^* levels. Thus in the chromium derivatives we anticipate two charge-transfer transitions. However for the d^4 and d^5 systems, there are a larger number of spin and orbitally allowed charge-transfer transitions. One-electron excitation from the metal t_{2g} level to, for example, the t_{1u} ligand level will give rise to more than one observed transition. However since the interelectronic repulsion energy is small, these various transitions can be expected to lie close together and to overlap.

Since the degree of back-donation is expected to increase with the number of d electrons, increasing stabilization of the t_{2g} levels from titanium through vanadium to chromium will provoke an increase in the charge-transfer energies in this sequence. This is observed though the overall spread is smaller for the dinitrogen derivatives than for the carbonyl derivatives as anticipated on the basis of the above discussion. The stabilization due to the change in mean spin pairing energy[18] (Table I) will also favor the same sequence of charge-transfer energies.

Turning now to the detailed assignments, we have been guided by a number of observations. In the d^6 complexes, the separation between the two charge-transfer transitions to the ligand π^* levels is of the order of 8700–9740 cm^{-1}. The separation depends in part upon the extent of π back-donation into the ligand.[20] Therefore we anticipate a smaller separation in the hexakis(dinitrogen) derivatives and a smaller separation in the carbonyl derivatives of the earlier transition elements.

Titanium Complexes

The charge-transfer spectra of the titanium carbonyl and hexakis(dinitrogen) complexes are very closely similar. Two bands are observed with the higher energy band being the least intense in both cases. These can be assigned to the one-electron electronic excitations to the t_{1u} and the t_{2u} levels, respectively. The bands are broad and presumably contain the various allowed excited states as indicated in Table IV. Both bands

in the carbonyl derivatives are shifted up some 25% in energy relative to the dinitrogen derivative.

Vanadium Compounds

At least four components can be seen under the broad envelope in both the carbonyl and dinitrogen complexes. We choose the lower two components as excitations to the t_{1u} level and the upper two components as excitations to the t_{2u} level. By use of the averages of these band energies the vanadium carbonyl transitions are shifted some 23–30% (Table V) relative to the dinitrogen derivatives.

Chromium Compounds

The two absorption bands near 300 nm in the dinitrogen derivative cannot be assigned to the two anticipated charge-transfer transitions since they lie too close together in energy. The two components are therefore to be assigned to a single electronic transition split perhaps by site asymmetry.

We assign this pair of transitions as excitation to the t_{2u} level and the weaker peak at 27 397 cm^{-1} as the transition to the t_{1u} level since this results in a shift of 28–30% of the band energies in the carbonyl complex relative to the dinitrogen complex. To assign the 27 397-cm^{-1} band as a d–d transition and the band at 40 000 cm^{-1} as the second main charge-transfer transition would make the chromium compound most atypical when compared with the titanium and vanadium derivatives. The shift in the first t_{1u} level in passing from dinitrogen to carbonyl would, with this latter assignment, be a mere 6% which seems improbably small. The band at 40 000 cm^{-1} is therefore assigned to the next charge-transfer state which is the t_{2g} π^* level and is expected to be weak.[20]

With the chosen assignments we obtain a consistent set of data in that (i) the carbonyl charge-transfer bands increase some 20–30% relative to the corresponding dinitrogen charge-transfer bands in all cases, (ii) there is an increase in the charge-transfer energy from titanium through chromium in both the dinitrogen and carbonyl cases but to a much greater degree in the latter, and (iii) the splitting between the two one-electron excitations (Table V) increases from titanium through chromium and increases from the dinitrogen to the carbonyl derivative.

Following the discussion of Gray and Beach,[20] the splitting between the two one-electron excitations is a measure in part of the ligand interaction energy and in part of the degree of back-donation from the metal to the ligand. Since the nitrogen orbitals will be more compact than the carbon monoxide ligand

orbitals, the interaction energy in the dinitrogen complexes should be smaller than that estimated (about 1000 cm^{-1}) in the carbonyl derivatives. As discussed above the degree of back-donation should be smaller for the dinitrogen complexes and this is in keeping with the smaller separation energy for this series. The increase from titanium through to chromium is also consistent with the increase in number of d electrons and/or stabilization of the t_{2g} d level.

Gray and Beach[20] also discussed the intensity of the second transition (to the t_{2u} level) as a measure of the extent of back-donation. The intensity of this band is, for example, much larger in the hexacarbonyl than in the hexacyanide derivatives where back-donation is relatively small. We note here that the intensity of the transition to the t_{2u} level in the carbonyl derivatives is the smallest for the titanium complex and largest for the chromium complex, in keeping with the extent of back-donation anticipated for this series. Exactly the same phenomenon is noticed for the hexakis(dinitrogen) complexes, the second band being least intense in the titanium compound and most intense in the chromium compound. Thus, by use of the assignments indicated in Table II, the data set are fully consistent with the theoretical expectations.

It must be cautioned, however, while the assignments seem acceptable, they must be considered as tentative in the absence of detailed absorption intensity data. Nevertheless the high degree of internal consistency does provide some guarantee that the low-energy absorptions are indeed crystal field in origin and not charge transfer as has been proposed by one group[21] for $Cr(CO)_6$.

Discussion

Our interpretation of the data leads to the conclusion that the nitrogen molecule in these complexes is acting as a relatively weak ligand compared to that of carbon monoxide. The extent of π back-donation is undoubtedly less than with carbon monoxide and the extent of σ donation would also be less in view of the tightly bound nature of the nitrogen σ pair of electrons. This gives rise to a Dq value for nitrogen which is considerably below that of carbon monoxide (Table III).

It is still necessary to explain why the charge-transfer transitions lie at lower energy in the N_2 derivatives.

The charge-transfer transition involves excitation from a π-bonding-stabilized t_{2g} orbital to the LUMO (π^*) orbital on N_2 or CO. Accepting that CO is a better π acceptor than dinitrogen will lead to a predicted greater stabilization of the metal t_{2g} set with the former ligand. This increased stabilization will contribute, in part, to placing the carbonyl charge-transfer transitions ($t_{2g} \rightarrow \pi^*$) at higher energy.

However a second-order mixing process must also be considered. Persuing a valence-bond formalism, second-order mixing of the state M^+L^- into the ground state $M-L$ ($L = N_2$ or CO) will result in the destabilization of the excited, charge-transfer state, ψ_{CT}, and stabilization of the ground state. Such mixing is inversely dependent on the separation of the states concerned and is dependent on the magnitude of the off-diagonal element which may be written $\langle t_{2g}|H|1\pi_g \rangle$. For reasons discussed in detail by Fenske and co-workers[12] relating to relative metal–ligand overlap, this off-diagonal element will be considerably larger for the carbonyl than for the dinitrogen system. This mechanism results in an increase in the charge-transfer transition energy relative to the ground state. The greater second-order interaction for the carbonyl ensures that the charge-transfer transition energy should indeed be greater than for the dinitrogen derivatives as is observed. The greater mixing of M^+L^- into the ground state of the carbonyl complex, relative to the situation in the dinitrogen complex, also explains the greater importance of π back-donation in the carbonyl systems. We have the rather intriguing consequence that *the lower the first-order energy of the acceptor orbital*

and the better its overlap, the greater the degree of back-donation in the ground state and the higher the energy of the charge-transfer excited state. We conclude that the charge-transfer data are indeed in accord with the greater degree of back-donation in the carbonyl derivatives.

The smaller degree of second-order mixing in the case of the dinitrogen complexes will ensure that the dinitrogen ligand will carry more negative charge in its excited charge-transfer state than will the carbonyl.

We advise caution in using the above generalization to predict relative π-bonding capabilities. In this case the better π acceptor, CO, has the larger charge-transfer energy, because the destabilization due to mixing is considerably more important than the differences in the π^*-orbital energies. This will not always be true. For example complexes of RNC (R is an alkyl group) have charge-transfer spectra at higher energies than comparable complexes of ArNC (Ar is an aryl group), e.g., with $Mn(I)$.[22,23] Yet we may safely conclude that ArNC is a better π-acceptor ligand than RNC. In this case greater destabilization of the $Mn^{2+}(ArNC)^-$ state is insufficient to overcome the initial much greater energy of $\pi^*(RNC)$ relative to $\pi^*(ArNC)$.

We conclude that all the available chemical and spectroscopic data are explainable in terms of N_2 being a weaker ligand than CO, i.e., a poorer σ donor and a poorer π acceptor. This is in accord with the low Dq values for the former ligand and with their comparative insensitivity to the metal in this series. It is also in agreement with the difficulty in binding dinitrogen to a metal in the first place.

However we also emphasize that the charge-transfer states of metal–dinitrogen complexes are energetically more accessible than those of the carbonyl derivatives and point out that the N_2 ligand in such states will be quite basic. This suggests that, in order to "fix" nitrogen, investigators should turn their attention to the chemistry of photochemically activated charge-transfer states.

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Reductions of Hexabromoiridate(IV) by Chromium(II) and by Pentacyanocobaltate(II). Evidence for Bromide-Bridged Binuclear Intermediates[1]

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The reaction between hexabromoiridate(IV) and chromium(II) proceeds in two stages and produces, ultimately, $IrBr_6^{3-}$ and $Cr(H_2O)_6^{3+}$ in ~60% yield and $IrBr_5(H_2O)^{2-}$ and $Cr(H_2O)_5Br^{2+}$ in ~40% yield. In the first stage, too fast to be measured ($k > 10^6$ M^{-1} s^{-1}), Ir(IV) and Cr(II) react via parallel inner-sphere and outer-sphere pathways. The outer-sphere reaction yields $IrBr_6^{3-}$ and $Cr(H_2O)_6^{3+}$. The inner-sphere path produces an intermediate identified as the successor complex $Br_5Ir^{III}BrCr^{III}(H_2O)_5$, which decomposes with a rate constant of 0.65 s^{-1} at 25 °C and 1.0 M ionic strength and associated activation parameters $\Delta H^\ddagger = 17.0 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = -2.4 \pm 1.8$ eu. The binuclear intermediate dissociates via parallel bond-rupture processes. Cr–Br bond rupture yields $IrBr_6^{2-}$ and $Cr(H_2O)_6^{3+}$, whereas Ir–Br bond rupture produces $IrBr_5(H_2O)^{2-}$ and $Cr(H_2O)_5Br^{2+}$. The $Co(CN)_5^{3-}$–$IrBr_6^{2-}$ reaction also proceeds in two stages. The first, too fast to be measured ($k > 10^6$ M^{-1} s^{-1}), corresponds to an inner-sphere reaction and yields an intermediate identified as the successor binuclear complex $Br_5Ir^{III}BrCo^{III}(CN)_5^{5-}$. The intermediate decomposes via parallel Ir–Br and Co–Br bond-rupture processes to produce $IrBr_6^{3-}$ and $Co(CN)_5(H_2O)^{2-}$ in 58% yield and $IrBr_5(H_2O)^{2-}$ and $Co(CN)_5Br^{3-}$ in 42% yield. The rate constant for the decomposition of the intermediate at 25 °C and ionic strength 0.10 M is 5.6 s^{-1} with $\Delta H^\ddagger = 14.9 \pm 0.4$ kcal/mol and $\Delta S^\ddagger = -5.1 \pm 1.2$ eu. The mechanisms of these reactions are compared with those of the analogous $IrCl_6^{2-}$–Cr^{2+} and $IrCl_6^{2-}$–$Co(CN)_5^{3-}$ reactions.

Detailed investigations of ligand-bridged binuclear intermediates, which persist for some time following an inner-sphere electron-transfer process, have been reported only in few instances. The detection of chloride-bridged successor complexes in the reduction of hexachloroiridate(IV) by chromium(II)[2,3] or pentacyanocobaltate(II)[4] has added to our understanding of the mechanism of oxidation–reduction reactions. In particular, the kinetic and stoichiometric studies of the dissociation of the binuclear complexes have given considerable insight into the factors that govern whether there is net transfer of the bridging ligand from oxidant to reductant in the overall redox reaction. In order to extend the scope of these studies, we have investigated the reduction of hexabromoiridate(IV) by chromium(II) and by pentacyanocobaltate(II).

Experimental Section

Materials. Sodium perchlorate was prepared by neutralization of sodium carbonate with perchloric acid and was recrystallized three times. Chromium(II) perchlorate solutions were prepared by reduction of solutions of chromium(III) perchlorate of known concentration with amalgamated zinc. Pentacyanocobaltate(II) solutions were prepared by addition of cobalt(II) perchlorate solutions to solutions containing the desired amounts of sodium cyanide, sodium hydroxide, and sodium perchlorate. All manipulations with oxygen-sensitive reagents were carried out under an atmosphere of purified argon.[4] Glass syringes and Teflon needles were used for transferring reagents anaerobically.

Samples of K_2IrBr_6 were prepared from $Na_2IrCl_6\cdot6H_2O$ (Alfa Inorganics) and from impure samples of K_2IrBr_6 (Platinum Chemicals). $Na_2IrCl_6\cdot6H_2O$ (1.6 g) was treated with 30 mL of 40% hydrobromic acid and 10 mL of bromine, and the mixture was allowed to reflux for 12–14 h. Most of the hydrobromic acid was neutralized by adding 50% potassium hydroxide, and then 15 mL of a saturated potassium acetate solution was added. The solid obtained was separated by decantation and washed several times with carbon tetrachloride and then with ethanol. The resulting solid was treated with 10 mL of 40% hydrobromic acid and 6 mL of bromine, and the mixture was allowed to reflux for 12–14 h. The fine, dark purple

crystals were decanted, washed with carbon tetrachloride and then with ethanol, and finally dried by suction. The same procedure was used when K_2IrBr_6 was used as the starting material, except that the first refluxing was carried out in the presence of 45 mL of water. The equivalent weight of the samples of K_2IrBr_6 used, measured by reaction with excess iodide followed by titration of the triiodide formed with thiosulfate, was 752 ± 1, as compared to 749.9 calculated for pure K_2IrBr_6.

Solutions containing the hexabromoiridate(III) ion were obtained by in situ reduction of $IrBr_6^{2-}$ with the equivalent amount of ascorbic acid.

Kinetic Measurements. For measurements of the $IrBr_6^{2-}$–Cr^{2+} reaction, solutions of $IrBr_6^{2-}$ with the desired amounts of $HClO_4$ and $NaClO_4$ were mixed in a stopped-flow apparatus with solutions of Cr^{2+} containing the same amounts of $NaClO_4$ and $HClO_4$. The disappearance of the intermediate produced was monitored at several wavelengths in the 500–265-nm region, and the absorbance vs. time data, collected in a 1800 IBM computer interfaced to the stopped-flow apparatus, were fitted by a nonlinear least-squares program to eq 1,

$$A_t = A_\infty + (A_0 - A_\infty) \exp(k_{obsd}t) \tag{1}$$

where A_0, A_t, and A_∞ are the absorbances at time 0, t, and after 8–10 half-lives, respectively, and k_{obsd} is the first-order rate constant for the decomposition of the intermediate. The rate constant for the decomposition of the intermediate produced in the $IrBr_6^{2-}$–$Co(CN)_5^{3-}$ reaction was obtained following the procedure outlined above, except that solutions of $IrBr_6^{2-}$ and Co^{2+} with the desired amount of $NaClO_4$ were mixed with solutions of NaCN and NaOH containing the same amount of $NaClO_4$. $Co(CN)_5^{3-}$ was maintained in excess over $IrBr_6^{2-}$ to avoid the slower reduction of $IrBr_6^{2-}$ by cyanide ion.

The rate of aquation of $IrBr_6^{3-}$ (eq 2) was measured spectro-

$$IrBr_6^{3-} + H_2O = IrBr_5OH_2^{2-} + Br^- \tag{2}$$

photometrically using a Cary 14 spectrophotometer. Two different procedures were employed. In the continuous-monitoring procedure, solutions containing the desired amounts of $IrBr_6^{3-}$, $HClO_4$, and $NaClO_4$ were placed in a cell in the thermostated compartment of the spectrophotometer, and the increase in absorbance at 375 or 436