length changes in Fe(III) complexes than is the case for similar Fe(II) compounds. Unfortunately, reasonable estimates of force constants and Δ values are as yet unavailable for complexes of the former ion. However, the present model suggests that for the same value of m the most important factor influencing bond length changes would be the ratio Δ/f, so that the experimental observations could be explained if f increases by a significantly greater amount than Δ, on going from the iron(II) to the iron(III) species. It is noteworthy that smaller structural changes are in general predicted for compounds involving ligands that form strong bonds but produce a relatively small splitting of the d orbitals such as might be the case for some sulfur-donor ligands. Substitution of the data appropriate to the $Co(NH_3)_6^{3+}$ ion into eq 1 ($m = 2$, $\Delta = 21\,000$ cm^{-1},[1] $f = 2.49$ mdyn/Å,[8] $r_0 = 1.97$ Å[13]) yields a value or $r_0 \simeq 2.11$ Å for the bond length predicted for the high-spin form of this ion. This is very similar to the value of 2.114 Å observed[14] for the high-spin $Co(NH_3)_6^{2+}$ ion, which is in agreement with the suggestion[15] that for complexes involving non-π-bonding ligands a change in the charge on the metal has little effect on the metal–ligand bond distance.

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Appendix

Consider two electron configurations of a metal complex differing in the distribution of m electrons between d orbitals separated in energy by an amount Δ. The energy of the second configuration relative to the first at bond length r_0 is given by

$$U = m\Delta + S$$

where S represents any contribution due to interelectron repulsion terms such as the so-called spin-pairing energy. Consider the effect of an expansion Q in the totally symmetric stretching mode of force constant f.[16] With the assumption that Δ is inversely proportional to the nth power of the bond length

$$U = \frac{f}{2}Q^2 + m\Delta\left[\frac{r_0 + CQ}{r_0}\right]^{-n} + S$$

where C is a normalization constant. For small values of CQ/r_0

$$U \simeq \frac{f}{2}Q^2 + m\Delta\left[1 - \frac{nCQ}{r_0}\right] + S$$

The displacement Q corresponding to a mininum energy of the second electron configuration is obtained by setting $\mathrm{d}U/\mathrm{d}Q = 0$, and as to a first approximation S is independent of Q, this gives

$$Q = \frac{mnC\Delta}{fr_0}$$

The change in each bond length is given by $\delta r = CQ$, where for the totally symmetric mode $C = 1/N^{1/2}$, N being the number of ligand atoms. It therefore follows that

$$\delta r = \frac{mn\Delta}{fr_0N}$$

Note that for both Δ and f the appropriate values are those of the initial state of bond length r_0.

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(13) This represents an average Co(III)–NH_3 bond distance; see ref 8, p 87.

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(16) The bond length change is conveniently calculated in Å with use of the relationship 1 mdyn/Å = 0.5035 × 10^5 cm^{-1} Å^{-2}.

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Polarized Crystal Spectrum of $Ni(NH_3)_4(NO_2)_2$: Non-"d-d" Assignment of the Band Centered at 20 000 cm^{-1}

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As part of a general investigation of the electronic and structural properties of transition-metal nitrite complexes, we have measured[1] the electronic spectrum of the (001) crystal face of the trans nitro complex $Ni(NH_3)_4(NO_2)_2$ at 10 K (see Figure 1); the room-temperature spectrum has been reported previously by Hare and Ballhausen.[2] The crystal structure of the compound has been described by Porai-Koshits[3] and, more recently, by Figgis et al.[4] The spectrum is conveniently discussed in terms of three regions, considered in order of decreasing energy (see Table I).

Region I (26 000–28 000 cm^{-1}). The b spectrum consists of three progressional band systems, each of interval 620 ± 25 cm^{-1}. Only two peaks can be resolved in the more intense a spectrum, with the lower energy one almost coinciding in position with that in b polarization. In this region the spectrum is quite similar to that reported[5] for $NaNO_2$, which shows a series of progressions of interval 632 ± 4 cm^{-1} assigned to the nitrite wagging mode δ_{NO_2} (ground-state energy 829 cm^{-1}) built upon an origin at 25 977 cm^{-1} and involving the excitation of single quanta of various lattice modes. In the case of $NaNO_2$ there has been general agreement that the overall band is due to the $^1B_2 \leftarrow {}^1A_1$ nitrite n $\rightarrow \pi^*$ transition. However, the nature of the nonbonding orbital has been the subject of debate. Early work[5] suggested that this was localized largely on the nitrogen atom, and this view was supported by Fee et al.[6] who observed an analogous band in several chromium(III) nitrito complexes. Recent calculations[7] and the behavior of the n $\rightarrow \pi^*$ band in various hydroxylic solvents[8] both suggest that the nonbonding orbital is localized largely on the oxygen atoms. If, as seems likely, the band in $Ni(NH_3)_4(NO_2)_2$ is due to the same transition as that in $NaNO_2$, then the latter propositon seems more plausible, as in the nickel complex the nitrogen lone-pair electrons are involved in bonding to the metal. This interpretation then assigns the peaks in region I of the spectrum of $Ni(NH_3)_4(NO_2)_2$ to an n(O) $\rightarrow \pi^*$ internal nitrite transition involving progressions in the nitrite wagging mode δ_{NO_2}, built upon an electronic origin at 26 260 ± 5 cm^{-1} and with the additional excitation of one quantum of vibrational modes of energy ~260 cm^{-1} (b system 3), 440 cm^{-1} (b system 2), and ~310 cm^{-1} (a). The vibrations of energy 260 and 310 cm^{-1} are likely to be metal–nitrite stretches or bends, while that of energy 440 cm^{-1} must be due to the metal–nitrite wagging mode ρ_w, which characteristically occurs at 450 cm^{-1} in nickel(II) nitro complexes.[9]

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(1) The compound was prepared by the method in W. G. Palmer, "Experimental Inorganic Chemistry", Cambridge University Press, New York, 1954, p 559. Physical measurements were made with use of a Cary 17 spectrophotometer and a Cryodine Model 21 cryostat.

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Table I. Energies of the Peak Maxima (cm^{-1}) Observed in the Electronic Spectrum of a Crystal of $Ni(NH_3)_4(NO_2)_2$ with the Electric Vector Parallel to the *a* and *b* Crystal Axes Measured at 10 K

region I				region II			region III		
b				*b*			*b*		
system 1	system 2	system 3	*a*	system 1	system 2	*a*	system 1	system 2	*a*
28 102	27 910	27 747	26 575	~22 880	20 620	~21 415	13 530	12 350	11 700
27 457	27 285	27 100	26 264	22 472	19 940	20 880	13 105	~11 750	
26 835	26 681	26 497		22 026	19 420	20 200			
26 255				21 589	18 710	19 705			
					18 130	19 085			
					~17 330	~18 380			

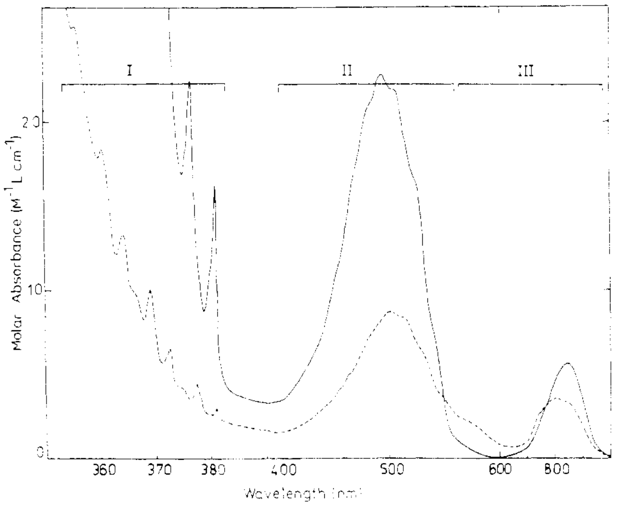

Figure 1. Electronic spectrum of a crystal of $Ni(NH_3)_4(NO_2)_2$ with the electric vector parallel to the *a* (full line) and *b* (dashed line) crystal axes measured at 10 K. Note the change in wavelength scale at 390 and 600 nm. See text for a discussion of regions I, II, and III.

Region II (17 000–23 000 cm^{-1}). The main band in this region exhibits poorly resolved vibrational fine structure in both polarizations with, in the *b* spectrum, a series of additional weak sharp peaks (system 2) built on an origin at 21 589 cm^{-1}. The latter progression has an interval of 430 ± 15 cm^{-1} and is most likely due to the "d–d" transition $^1A_{1g} \leftarrow {}^3A_{2g}$ coupled with the metal–nitrite wagging mode ρ_w. The progressional interval on the main band is ~630 cm^{-1}, which seems too high in energy for any metal–ligand vibration. The close similarity to the spacings observed for the n → π^* band discussed above suggests, rather, that the bulk of the intensity derives not from the $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ "d–d" transition, as had previously been supposed in this[2] and related compounds,[10] but from a transition in which an electron is excited into the nitrite π^* orbital. It may be noted that there have been suggestions that the analogous peak in the spectrum of the $Ni(NO_2)_6^{4-}$ ion is probably not "d–d" in origin.[11] Two assignments of the band seem plausible. It could be due to the spin-forbidden analogue of the n → π^* internal nitrite transition, with an intensity enhanced by the high spin–orbit coupling constant of the nickel(II) ion. A peak assigned in this manner has been observed centered at ~23 000 cm^{-1} both in $NaNO_2$ itself[12] and in several nickel(II) complexes containing chelated nitrite ions.[13] The low energy of the band at ~20 000 cm^{-1} in $Ni(NH_3)_4(NO_2)_2$ argues against such an assignment, as in this complex the origin of the spin-allowed n → π^* transition is actually slightly higher in energy than those in $NaNO_2$[5] and the nickel(II) complexes containing chelating nitrites.[13] Also, the relatively high intensity of the band at ~20 000 cm^{-1} seems incompatible with an assignment as a spin-forbidden internal nitrite transition. Although this might be enhanced by the $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ "d–d" transition, which must contribute to the absorption in the region, in certain other nickel nitro complexes the "d–d" transition can actually be resolved at lower energy than the peak at ~20 000 cm^{-1}, showing that the latter band is indeed quite intense with an absorbance greater than that of the "d–d" peak.[11] It therefore seems more likely that the band at ~20 000 cm^{-1} is due to a metal → nitrite π^* electron transfer transition. A similar assignment has been proposed[14] for bands centered at 21 000–23 000 cm^{-1} in the hexanitro complexes of Pb^{2+}, Bi^{3+}, and Ce^{3+}. The intensity might seem rather low for a charge-transfer band, but the transition presumably involves excitation from the metal e_g orbitals into the nitrite π^* orbital, and these are orthogonal in the absence of vibronic coupling. The fact that the band at ~20 000 cm^{-1} is not observed in complexes where nickel(II) is coordinated to nitrite via oxygen is consistent with the above assignment, as the nitrite π^* orbitals are only directed toward the metal when this ligand bonds via nitrogen.

Region III (10 000–17 000 cm^{-1}). The main absorption in this region may be assigned to the transition $^3T_{2g} \leftarrow {}^3A_{2g}$ split by low symmetry components of the ligand field (the weak sharp peaks at 13 105 and 13 530 cm^{-1} are probably associated with the $^1E_g \leftarrow {}^3A_{2g}$ transition). The molecular point group of the complex is D_{2h}, though if the π interaction with the nitrite is assumed to be isotropic about the metal–nitrite bond axis, as has been done in the past,[2,10] this rises to D_{4h}. In either approximation, one transition is expected at exactly Δ for the ammonia groups, and it seems likely that this gives rise to the band centered at 11 700 cm^{-1} in both polarizations; this is slightly higher in energy than the value Δ = 11 100 cm^{-1} observed[15] for the $Ni(NH_3)_6^{2+}$ ion. If the microsymmetry is taken to be D_{4h}, the energy of the peak at 12 350 cm^{-1} in *b* polarization can be used to estimate[16] a value of Δ = 12 950 cm^{-1} for the nitro groups in the complex, in good agreement with that reported[11] for the $Ni(NO_2)_6^{4-}$ ion. It is apparent that the nitro groups in $Ni(NH_3)_4(NO_2)_2$ exert a significantly stronger ligand field than the ammine ligands, despite a greater Ni–N bond length ($Ni–NO_2$ = 2.142 Å, $Ni–NH_3$ = 2.109 Å).[4] However, it is as yet impossible to say whether this is caused by a stronger σ interaction, or because the nitrite functions as a π acceptor, or a combination of these factors. It should be noted that previous interpretations of the electronic spectra of nickel nitro complexes in terms of ligand field splitting parameters[2,10] are rendered invalid by the present assignment of the 20 000-cm^{-1} band as due to a non-"d–d" transition.

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Crystal Structure of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$. A 4-fold Disordered Structure in a Crystal Isomorphous with $Fe_3(CO)_{12}$

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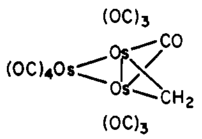
The protonation of $[Os_3(CO)_{11}(CHO)^-]$ has been shown to give rise to a neutral complex of stoichiometry $Os_3(CO)_{11}(CH_2)$. Steinmetz and Geoffroy[1] have proposed a structure for this complex in which a bridging methylene and a bridging carbonyl group span one edge of the triangular Os_3 framework (I). The two bridging groups are each of considerable contemporary interest, for the following reasons: (1) Bridging methylene groups are implicated as intermediates in such processes as the Fischer–Tropsch synthesis.[2] (2) Bridging carbonyl groups are extremely rare in osmium carbonyl chemistry. To the best of our knowledge $Os_3(CO)_{10}(PhC_2Ph)$[3] is the only trinuclear osmium carbonyl derivative shown crystallographically to have a bridging carbonyl ligand and here it is an *asymmetric* bridge.



I

Johnson[4] has commented that the Os_3 triangle cannot be accommodated in the cavity formed by an icosahedral arrangement of CO groups, so that $Os_3(CO)_{12}$ has an (all terminal) anticuboctahedral arrangement of carbonyl ligands in contrast to the icosahedral arrangement (ten terminal, two bridging) in $Fe_3(CO)_{12}$.

We initially began this study in 1979. We outline below the key steps in solving this 4-fold disordered structure and the chemical information obtainable therefrom.

Experimental Section

A. Data Collection. Deep red, well-formed crystals of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ were provided by Professor G. R. Geoffroy. An irregular fragment, cleaved to an average dimension of ~0.1 mm, was sealed into a glass capillary and was used for all measurements. Description of our operation of the Syntex $P2_1$ diffractometer has been published;[5] details of the present analysis are in Table I.

Table I. X-ray and Crystal Parameters for $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$

(A) Crystal Parameters[a] at 23 (1) °C

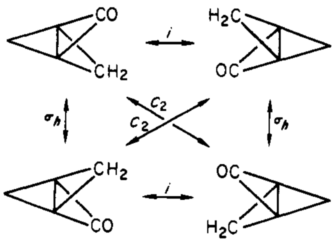
crystal system: monoclinic
space group: $P2_1/n$
mol wt = 892.6
ρ(calcd) = 3.39 g cm^{-3}
$Z = 2$
$a = 8.5620$ (14) Å
$b = 11.2352$ (22) Å
$c = 9.1486$ (16) Å
$\beta = 96.274$ (13)°
$V = 874.8$ (3) Å

(B) Intensity Data

radiation: Mo Kα [$\bar{\lambda} = 0.710\,730$ Å]
2θ range: 3.0–45.0°
scan type: θ(crystal)–2θ(counter)
scan speed: 2.00° min^{-1}
scan range: $[2\theta(K\alpha_1) - 1.0]° - [2\theta(\alpha_2) + 1.0]°$
reflctns measd: $\pm h + k \pm l$ (2 forms)
reflctns collected: 2153 collected yielding 1153 independent data
abs coeff: 258 cm^{-1}

[a] Based on a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ peaks of 24 reflections with $2\theta = 20–30°$.

Scheme I



Two complete asymmetric units of diffraction data were collected. The intensities were corrected for absorption by an empirical ψ-scan method; six curves were used with $(I_{max})/(I_{min})$ values in the range 1.18–1.40. Data averaging, as well as all subsequent calculations, utilized the Syntex XTL program package as modified at SUNY-Buffalo.

B. Solution and Refinement of the Structure. The use of direct methods (MULTAN)[6] followed by an "*E* map" revealed immediately that the structure was disordered. A "Star-of-David" pattern, characteristic of a triangular cluster disordered about a crystallographic inversion center, was found about the positions (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$) in space group $P2_1/n$. From this point, the complete solution of the structure proceeded very slowly since there was no certainty *at this time* of the exact connectivity of ligands in the complex. The completion of the structural study was aided immensely by two occurrences: (1) the proposal, by Steinmetz and Geoffroy, of structure I for the complex and (2) the belated realization that the present structure is not only similar to but actually *isomorphous* with $Fe_3(CO)_{12}$.[7–9]

The computational steps essential to solution of this structural problem were as follows.[10]

(1) The three crystallographically independent osmium atoms were assigned occupancies of $^1/_2$, and their positional and anisotropic thermal parameters were refined.

(2) Six crystallographically independent oxygen atoms were located from a difference-Fourier synthesis, and their positional and anisotropic

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[8] It is interesting to note that the structure of $Fe_2(CO)_8(\mu\text{-}CH_2)$ is disordered and is isomorphous with $Fe_2(CO)_9$.[9] See: Meyer, B. B.; Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1981**, *20*, 3024.

[9] (a) The initial solution of the structure of $Fe_2(CO)_9$ is reported in: Powell, H. M.; Ewens, R. V. G. *J. Chem. Soc.* **1939**, 286. (b) The structure was later redetermined: Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* **1974**, 800.

[10] The reader will note similarities to the solution of the structure of disordered $Ir_4(CO)_{12}$: Churchill, M. R.; Hutchison, J. P. *Inorg. Chem.* **1978**, *17*, 3528.

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