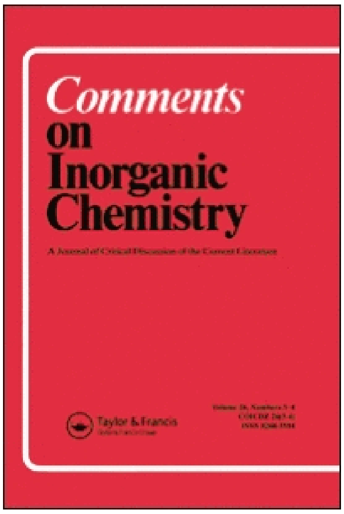

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Charge Transfer Energies of Metal Complexes. Nature of the Lowest Charge Transfer Excited State of Hexacyanocobaltate(1ll)

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Charge Transfer Energies of Metal Complexes. Nature of the Lowest Charge Transfer Excited State of Hexacyanocobaltate(III)

The principles underlying correlations of charge transfer energies for related metal complexes are examined in light of data that have become available in recent years. As a consequence, the charge transfer absorption band of $Co(CN)_6^{3-}$ at 50,600 cm^{-1} is assigned to a $\sigma(CN) \rightarrow d\sigma^*(Co)$ transition.

Over 20 years ago, one of us commenced[1] a study of the electronic spectra of metal complexes of simple carbon-donor ligands (e.g., CN^-, CO, and cyclopentadienide[2] (cp)). For some complexes, "ligand–field" (d–d) transitions were apparent, but in essentially all cases very intense bands were observed, for which ligand-to-metal (LMCT) and metal-to-ligand (MLCT) charge transfer assignments were proposed. Identifying the specific transitions in these charge transfer spectra has been a difficult but not unrewarding task that has been the main basis for our ongoing collaboration.

The oldest assignments have, in the main, withstood the test of time. One of them, however, has troubled us over the years for various reasons. The nominal purpose of this Comment is to modify that assignment. The real purpose is to review some of the empirical approaches we developed, as data accumulated, for predicting the energies of charge transfer transitions. While economical *ab initio* calculations do not even now predict charge transfer excitations with any accuracy,[3] we think that charge transfer as-

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signments of experimental spectra can and should be far from arbitrary, as extensive reliable correlations are available.

The historical basis of the problem is that the $Co(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ ions show, in addition to obvious d–d transitions, intense bands at, respectively, 50,600 (ϵ 35,400) and 45,900 cm^{-1} (ϵ 24,200). (Hereafter we will represent energy and intensity data such as the latter entry as "45.9 (24,200)," with implied units.) It seemed reasonable to assign these bands to similar transitions, and the red shift for Fe^{II} versus Co^{III} then "unambiguously" indicated an MLCT assignment, as an increase of central nuclear charge for isoelectronic complexes should shift MLCT to higher energy[1]; the opposite effect occurs for LMCT.[4]

The $Fe(CN)_6^{4-}$ MLCT assignment has subsequently found strong support in photoionization studies that show an intense ionization cross-section maximum at ~46.[5] As emphasized by Delahay,[5] ionization energy and bandshape considerations strongly indicate that the photoinduced process occurs from a *bound* state. An MLCT state is then reasonable (whether or not metal $(n + 1)$p orbital mixing is important), because of the diffuse nature of the orbital populated in the excited state. Rationalization of net electron ejection from an LMCT state would not be straightforward.

Further support comes from the observation that $Ru(CN)_6^{4-}$ and $Os(CN)_6^{4-}$ have very similar bands at 48.8 (37,000)[6] and 47.0 (47,400),[1] respectively. Rough invariance down a column of the periodic table for valence-isoelectronic complexes is now recognized to be a common feature of MLCT transitions involving $d\pi \rightarrow \pi^*$(ligand) excitations; the most thoroughly established examples are the *tris*(bpy) (bpy = 2,2′-bipyridine) complexes of Fe^{II} (18.6), Ru^{II} (21.6), and Os^{II} (14.8).[7]

On the other hand, LMCT transitions for octahedral d^6 complexes strongly blue-shift down a column. Consider σ(I)-LMCT for the $M(CN)_5I^{3-}$ complexes of Co^{III} (38.5), Rh^{III} (45.5), and Ir^{III} (51.3).[8] The reason for the difference in behavior appears to be that 10 Dq (the $d\pi$–$d\sigma^*$ splitting) greatly increases down a column (as is independently known from d–d spectra), but the energy of $d\pi$ is much less dependent than is that of $d\sigma^*$. Energies of $\sigma(L) \rightarrow d\pi$ LMCT also remain roughly constant for the $(d\pi)^5$ series $[(Fe, Ru, Os)(CN)_6]^{3-}$ at 23.8, 21.7, and 24.3,[1,6] consistent with this idea. Note that both MLCT and $\sigma(L) \rightarrow d\pi$ LMCT series suggest that the second-row dπ is slightly stabilized relative to the first row, but that the third-row dπ level is then destabilized; the lanthanide contraction strikes again.

Thus, the interpretation of the $Fe(CN)_6^{4-}$ spectrum seems secure. But the situation is entirely different when we consider the $Co(CN)_6^{3-}$ assignment. First of all, photoionization has not been observed from the $Co(CN)_6^{3-}$ charge transfer state.[9] Moreover, available photochemical data suggest that charge transfer excitation yields products (Co^{II} and CN radical degradation species) that are more easily rationalized in terms of the reactions of LMCT states.[10]

Data for charge transfer shifts down a periodic table column initially seemed ambiguous, as the available UV spectra of Rh^{III} and Ir^{III} hexacyanides had ill-defined absorption features.[1] However, subsequent efforts have shown that this UV absorption was primarily due to impurities,[8(a),11] and that the charge transfer that corresponds to the intense band of $Co(CN)_6^{3-}$must be strongly blue-shifted (into the vacuum UV) for both $Rh(CN)_6^{3-}$ and $Ir(CN)_6^{3-}$.

These data qualitively indicate that a $\sigma(CN) \rightarrow d\sigma^*(Co)$ assignment might be more appropriate for the $Co(CN)_6^{3-}$ charge transfer band. We will now show that this LMCT assignment is in fact the better choice.

First, consider the energy of the σ-LMCT for $Co(CN)_6^{3-}$. Because the lowest LMCT transition of $Fe(CN)_6^{3-}$, 23.8 (1100), is established[1,12] as $\sigma(CN) \rightarrow d\pi\ (Fe^{III})$, a crude estimate of the $\sigma(CN) \rightarrow d\sigma^*\ (Co^{III})$ energy may be obtained simply by adding 10 Dq for $Co(CN)_6^{3-}$, 34.5.[1] However, a correction must be made for spin pairing in the d^5 Fe^{III} LMCT transition. After Jørgensen,[4] we estimate the correction to be ~10. Thus the σ-LMCT energy for $Co(CN)_6^{3-}$ is predicted to be $(34.5 + 23.8 - 10) \simeq 48$.

We can improve on the spin-pairing energy estimate in the following fashion. The lowest energy LMCT transition of $Fe(cp)_2^+$, $\sigma\ (cp) \rightarrow d\pi$, is at 16.2 (450),[2] while $Co(cp)_2^+$ exhibits $\sigma(cp) \rightarrow d\sigma^*$ at 38.0 (38,000).[13] From analysis of the d–d spectrum, it is known[2] that the $d\pi - d\sigma^*$ splitting in $Co(cp)_2^+$ is 31.6. An estimate of the dπ spin-pairing energy for the cp complexes is therefore $31.6 - (38.0 - 16.2) = 9.8$. Since the spectroscopic properties of the cp and CN complexes indicate some similarity, taking the dπ spin-pairing energy as ~10 has independent support.

Evidently, ~48 is a good estimate of the σ-LMCT energy for $Co(CN)_6^{3-}$*, and the agreement with the observed charge transfer energy of 50.6 is satisfactory.*

We now turn to the question of where the lowest dπ → π*(CN) transition might appear for $Co(CN)_6^{3-}$, given that the 45.9 assignment is correct for $Fe(CN)_6^{4-}$. This is a much more difficult question, as variations in metal $(n + 1)$p mixing with π*(ligand) levels are likely to be of consequence for large changes in central metal charge.

Two comparisons are nonetheless available. First, consider $Fe(bpy)_3^{2+}$ (lowest MLCT at 18.6) and $Co(bpy)_3^{3+}$. The latter does not show any transitions attributable to MLCT, either by electronic absorption or CD, below ~27, where onset of strong ligand absorption occurs.[14] Thus, a blue shift of MLCT for Co^{III}/Fe^{II} of $\geqslant 8$ can be inferred.

Another estimate is obtained from the spectra of metal carbonyl complexes, for which the assignment of the intense ultraviolet absorptions to MLCT is established.[1(c)] The MLCT bands of $Mn(CO)_6^+$ are blue-shifted by ~7–9 relative to those of $Cr(CO)_6$.[1(c)]

Thus, a blue shift of $Co(CN)_6^{3-}$ MLCT by $\geqslant 8$ is expected by either comparison, thereby placing the lowest MLCT transition at >54.[15] Additional experiments no doubt will establish whether or not $Co(CN)_6^{3-}$ MLCT (or d → p) occurs in the vacuum-UV region near the predicted energy. Resolution of this question will determine exactly how far correlations such as those we have utilized can be pushed.

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References and Notes

1. (a) H. B. Gray and N. A. Beach, J. Am. Chem. Soc. **85**, 2922 (1963). (b) J. J. Alexander and H. B. Gray, *ibid.* **90**, 4260 (1968). (c) N. A. Beach and H. B. Gray, *ibid.* **90**, 5713 (1968).
2. Y. S. Sohn, D. N. Hendrickson and H. B. Gray, J. Am. Chem. Soc. **93**, 3603 (1971).
3. A. Aizman and D. A. Case, Inorg. Chem. **20**, 528 (1981).
4. C. K. Jørgensen, Prog. Inorg. Chem. **12**, 101 (1970).
5. (a) L. Nemec, L. Chia and P. Delahay, J. Phys. Chem. **79**, 2935 (1975) (b) L. Nemec and P. Delahay, J. Chem. Phys. **57**, 2135 (1972). (c) P. Delahay, Chem. Phys. Lett. **90**, 425 (1972).
6. (a) M. B. Robin, Inorg. Chem. **1**, 337 (1962). (b) F. M. Crean and K. Schug, *ibid.* **23**, 853 (1984).
7. (a) F. Felix, J. Ferguson, H. U. Güdel and A. Ludi, J. Am. Chem. Soc. **102**, 4096 (1980). (b) S. DeCurtins, F. Felix, J. Ferguson, H. U. Güdel and A. Ludi, *ibid.* **102**, 4102 (1980).
8. (a) G. L. Geoffroy, M. S. Wrighton, G. S. Hammond and H. B. Gray, Inorg. Chem. **13**, 430 (1974). (b) V. M. Miskowski and H. B. Gray, *ibid.* **14**, 401 (1975).
9. A. W. Adamson, Coord. Chem. Rev. **3**, 69 (1963).
10. (a) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, J. Am. Chem. Soc. **97**, 219 (1975). (b) R. Schwartz and K. Tede, Ber **60B**, 69 (1927).
11. The absorption spectrum of a highly purified sample of $K_3Ir(CN)_6$ in aqueous solution exhibits $\epsilon \sim 3500$ at 53.0, the experimental limit, with no sign of any incipient maximum (V.M.M., unpublished work).
12. R. Gale and A. J. McCaffery, J. Chem. Soc. Dalton Trans. 1345 (1973).
13. The LMCT assignment for $Co(cp)_2^+$ (Ref. 2) has been strongly supported by the work of Robbins (J. L. Robbins, N. Edelstein, B. Spencer and J. C. Smart, J. Am. Chem. Soc. **104**, 1882 (1982); J. L. Robbins (private communication). $Co(Me_5cp)_2^+$, with an electrochemical reduction potential 0.63 V more cathodic than $Co(cp)_2^+$, has its intense CT band at 34.2, strongly red-shifted from the $Co(cp)_2^+$ LMCT. Moreover, $Ni(Me_5cp)_2^{2+}$ has an analogous band at 31.8, red-shifted as expected because of increased central-atom charge.
14. (a) J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire and H. Lip, Inorg. Chem. **8**, 771 (1969). (b) L. S. Dollimore and R. D. Gillard, J. Chem. Soc. Dalton Trans. 933 (1973). (c) J. Josephson and C. E. Schaeffer, Acta Chem. Scand. Ser. A **A31**, 813 (1977).
15. We draw attention to the fact that an argument for MLCT given in Ref. 8(b) is far from compelling. It was suggested that the lack of notable wavelength shifts of the $Co(CN)_6^{3-}$ CT band upon monosubstitution was consistent with an MLCT assignment. This is indeed the case, but it is equally true that the energy of the strongest $\sigma(CN) \rightarrow d\sigma^*$ transition, being "equatorially localized," $(\sigma(CN^{eq}) \rightarrow d_{x^2-y^2})$, would also be relatively insensitive to axial substitution.