

Evidence for the Interaction of a Transition-metal Ion with the Oxygen Atom of a Terminal Metal Carbonyl Group

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Summary The complex $\text{Co}_3[\text{Fe}(\text{CN})_5\text{CO}]_2$ has been prepared and shown to contain a carbonyl group bonded to transition metals through both its carbon and oxygen atoms.

THE potentially bidentate ligand carbon monoxide has recently been shown to be capable of bonding through both its carbon and oxygen atoms. Shriver and his co-workers¹ have prepared adducts of triethylalane with $\text{Fe}_2(\pi\text{-C}_5\text{H}_5)_2(\text{CO})_4$ and $\text{Fe}_4(\pi\text{-C}_5\text{H}_5)_4(\text{CO})_4$, and Kotz and Turnipseed² have prepared the adduct of trimethylalane with $\text{Ph}_3\text{PC}_5\text{-H}_4\text{Mo}(\text{CO})_3$. In both these cases the carbon end of CO is bound to a transition metal, and the oxygen end to aluminium. We report here evidence for a series of complexes in which both ends of carbon monoxide are co-ordinated to transition metals.

Nitroprusside and its analogues, $\text{Fe}(\text{CN})_5\text{X}^{n-}$, form insoluble precipitates with transition-metal ions. I.r. and X-ray data indicate that in most cases the products adopt the Prussian blue structure.³⁻⁵ Since in such a structure all cyanides are bridging,⁶ the unique ligand X is forced into a bridging configuration. Consideration of likely bond distances⁷ for metal complexes of $\text{Fe}(\text{CN})_5\text{CO}^{3-}$ adopting the Prussian blue structure leads to the prediction of a metal-oxygen bond of approximately 1.9 Å, which must be considered bonding.

An aqueous solution of $\text{Na}_3\text{Fe}(\text{CN})_5\text{CO}^8$ was added to an excess of aqueous CoCl_2 . A green precipitate formed,

† The nitrogen value was slightly high, which may be due to partial decomposition to ferrocyanide, and would be consistent with the i.r. spectrum. Extensive decomposition can be ruled out on the basis of i.r. spectra and the observed Co/Fe ratio of 3/2.

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² J. C. Kotz and C. D. Turnipseed, *Chem. Comm.*, 1970, 41.

³ J. B. Ayres and W. H. Waggoner, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2045.

⁴ L. A. Gentil, E. F. Baran, and P. J. Aymonino, *Z. Naturforsch.*, 1968, **23b**, 1264.

⁵ E. L. Brown and D. B. Brown, unpublished observations.

⁶ A. Ludi, H. -U. Güdel, and M. Rüegg, *Inorg. Chem.*, 1970, **9**, 2224.

⁷ D. B. Brown and D. F. Shriver, *Inorg. Chem.*, 1969, **8**, 37.

⁸ W. Hieber, R. Nast, and C. Bartenstein, *Z. anorg. Chem.*, 1953, **272**, 32.

⁹ F. A. Cotton, R. R. Monchamp, R. J. M. Henry, and R. C. Young, *J. Inorg. Nuclear Chem.*, 1959, **10**, 28.

which, after drying at room temperature, analysed correctly for $\text{Co}_3[\text{Fe}(\text{CN})_5\text{CO}]_2 \cdot 5 \cdot 7\text{H}_2\text{O}$.† This compound had a face-centred-cubic lattice with $a = 10 \cdot 27$ Å, as expected for the Prussian blue structure.

I.r. spectra are consistent with the presence of a linear-bridged carbonyl. $\text{Na}_3\text{Fe}(\text{CN})_5\text{CO}$ exhibits bands at 2015(m), 2040(s), 2055(s), 2075(s,sh), and 2095(m,sh) cm^{-1} . Complex formation should separate the CO and CN stretches, since upon bridge formation cyanide frequencies increase, whereas carbonyl frequencies decrease.^{1,2} The complex exhibits a carbonyl stretch at 1950(m) cm^{-1} , and cyanide frequencies at 2025(m), 2090(s), 2120(s,sh), and 2185(w) cm^{-1} . Thus, the carbonyl oxygen atom in this complex is bonded to cobalt. Cotton⁹ reported an i.r. spectrum for $\text{K}_3\text{Fe}(\text{CN})_5\text{CO}$ very similar to what we observe for $\text{Na}_3\text{Fe}(\text{CN})_5\text{CO}$, and he assigned a band at 2052 cm^{-1} to the carbonyl stretch. However, on the basis of the frequencies and intensities in our materials and comparison with the spectrum of nitroprusside we prefer to assign the 2040 cm^{-1} absorption in $\text{Na}_3\text{Fe}(\text{CN})_5\text{CO}$ to this mode. Thus, the CO frequency decreases by 90 cm^{-1} upon bridge formation, which is similar to the decrease of 112 cm^{-1} observed by Shriver.¹

Preliminary evidence indicates that Mn^{2+} and Ni^{2+} complexes also contain linear-bridged carbonyl groups.

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