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Binuclear Complexes of Fe(III) and Cr(III) with Bridging Cyano Ligand

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Recently many binuclear complexes with bridging cyano group, which are of peculiar interest as possible intermediates in redox processes,[1] have been described. Our work on the ammine complexes of Cr(III)[2] offered the possibility of preparing and studying some binuclear derivatives of these complexes with the bridging cyano ligand.

Thus, we have obtained several complexes of this type with different metallic cations, according to the following equation:

$$[Cr(H_2O)_m(NH_3)_{6-m}]^{3+} + [M(CN)_6]^{n-}$$
$$\leftrightharpoons [Cr(H_2O)_{m-1}(NH_3)_{6-m}{-}NC{-}M(CN)_5]^{3-n}$$

in particular, the neutral complexes in which M = Fe (III) and m = 1, 2.

Previously, an analogous complex of formula $[Fe(CN)_5{-}CN{-}Cr(H_2O)_5]$ has been reported by J.P. Birk.[3]

We are working with other complexes in which M = Co, Cr and studying the thermal reactions of these binuclear complexes which lead to the formation of very stable polymers.

Experimental

Complex (I), $[Fe(CN)_5{-}CN{-}Cr(H_2O)(NH_3)_4]$

2 g of $[Cr(H_2O)_2(NH_3)_4{\cdot}(ClO_4)_3$[4] are dissolved in 20 ml of water acidified with acetic acid; 2 - 3 g of solid finely powdered $Na_3[Fe(CN)_6]$ are added with constant stirring until the new complex precipitates. Once filtered the complex is washed with cold water, ethanol and ether. *Anal.* Found: Cr(III), 14.76; NH_3, 19.26; $[Fe(CN)_6]^{3-}$, 59.25%. Calcd: Cr(III), 14.86; NH_3, 19.43; $[Fe(CN)_6]^{3-}$, 60.15%.

Complex (II), $[Fe(CN)_5{-}CN{-}Cr(NH_3)_5]\cdot H_2O$

3 g of $[Cr(H_2O)(NH_3)_5](NO_3)_3$[5] are dissolved in 50 ml of water at room temperature and 3 g of solid finely powdered $K_3[Fe(CN)_6]$ are added to the solution with constant stirring until the new complex precipitates. *Anal.* Found: Cr(III), 14.10; NH_3, 23.05; $[Fe(CN)_6]^{3-}$, 57.63%. Calcd: Cr(III), 14.15; NH_3, 23.19; $[Fe(CN)_6]^{3-}$, 57.74%.

Results and Discussion

The absorption maxima of the new compounds are presented in Table I. As can be seen in this table, the transition $\nu_1[^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)]$ of Cr(III) octahedral complexes, which for the $[Cr(H_2O)_2(NH_3)_4]^{3+}$ and $[Cr(H_2O)(NH_3)_5]^{3+}$ ions, appear at 494 and 480 nm, respectively, is shifted toward lower frequencies in the corresponding binuclear complex. Nevertheless at neutral pH or in aged solution, this transition appears again at 490 - 495 and 475 - 485 nm, due certainly to the cleavage of cyano bridge.

TABLE I. Electronic Spectra (maxima in nm).

$K_3[Fe(CN)_6]$	Complex I	Complex II
–	515[a]	515[a]
–	490 - 495[b,c]	475 - 485[b,c]
420	420	420
405	405	405
320	320	320
302	302	302
280[b]	280[b]	280[b]
260	260	260
216	216	210

[a] In freshly prepared solution or in acetic acid. [b] Shoulder. [c] In aged solution.

TABLE II. I.R. Spectra (cm^{-1}).

$K_3[Fe(CN)_6]$	Complex I	Complex II	Assg.
–	2137(w)	2144(w)	ν(–CN–)
2125(s)	2115(s)	2124(s)	ν(–CN)
511(w)	505(w)	515(w)	ν(Fe–CN)
387(s)	378(s)	395(s)	δ(Fe–CN)

It is well known that in complexes of the type M–CN–M′, the CN stretching band of the bridging cyano group absorbs at higher frequencies than the terminal cyano group.[6] Apart from the analytical data and conductivity measurements, the splitting of the CN stretching band as shown in Table II gives the best evidence of the existence of a bridging cyano group, as stated by many authors.[7]

The conductivity measurements lead to values of ionic mobilities in the range of 200 - 220 ohm^{-1} mol^{-1} cm^2, for freshly prepared solutions, and 600 - 620 for aged solutions (1 hour). These values, as compared with those of the mononuclear species,[8,9] together with the conductivity measurements at various times, indicate that the cleavage of the CN–M bond, by means of an aquation reaction, is very fast and practically complete in 1 hour.

References

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2 J. Casabó and J. M. Coronas, *An. Quim., 70,* 330 (1974); J. Casabó, J. M. Coronas and J. Ribas, *Inorg. Chim. Acta, 11,* 149 (1974); J. Casabó, J. Ribas and J. M. Coronas, *J. Inorg. Nucl. Chem.,* in press; J. Casabó, J. M. Coronas and M. Ferrer, *Inorg. Chim. Acta,* in press.

3 J. P. Birk, *J. Am. Chem. Soc., 91,* 3189 (1973).

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6 N. Nakamoto, "Infrared spectra of Inorganic and Coordination Compounds", 2nd ed., Wiley, New York (1970).

7 D. F. Shriver, *Struc. Bonding, 1,* (1966); H. J. Coerver and C. Curran, *J. Am. Chem. Soc., 80,* 3522 (1958).

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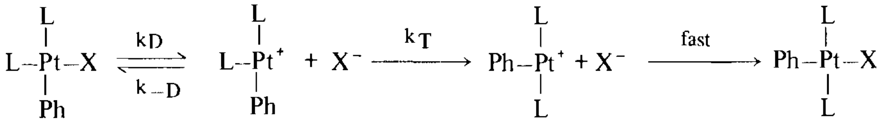
ERRATA to Volumes 14 and 15

Factors Affecting Dissociative and Associative Mechanisms on Platinum(II) Complexes

R. ROMEO, D. MINNITI and M. TROZZI, *14,* L15 (1975):

The reaction scheme should read:



$$\mathrm{L{-}\overset{L}{\underset{Ph}{Pt}}{-}X} \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} \mathrm{L{-}\overset{L}{\underset{Ph}{Pt^+}}} + X^- \xrightarrow{k_T} \mathrm{Ph{-}\overset{L}{\underset{L}{Pt^+}}} + X^- \xrightarrow{\text{fast}} \mathrm{Ph{-}\overset{L}{\underset{L}{Pt}}{-}X}$$

The Structure of Pd^{II} Complexes Containing the Tridentate Ligand Diethylenetriamine and its N-alkyl Derivatives. Part I. Molecular Structure of Nitrodiethylenetriaminepalladium(II) Nitrate and Nitro-1,1,7,7-tetraethyldiethylenetriaminepalladium(II) Nitrate

N. BRESCIANI, M. CALLIGARIS, L. RANDACCIO, V. RICEVUTO and U. BELLUCO, *14,* L17 (1975):

Line 9 from the bottom on page L18, left column should read:

"the normal orientation of the NO_2 group is preferred because of the steric repulsion between the NO_2 group and the"

Copper(II) Complexes of α-Oximinoketones

J. C. DANILEWICZ, R. D. GILLARD and R. WOOTTON, *15,* L5 (1975):

In the text to structure I on page L5, the correct version reads: (Ia) R_1 = Ph, R_2 = CH_3

Preparation and Doping of $CaLaZrTaO_7$ Pyrochlore

S. LARACH, *15,* L8 (1975):

The top paragraph, right column, should read:

"It is of interest that the material formed by cold-pressing contained *two* pyrochlore phases, in addition to ZrO_2. The major pyrochlore phase was the same as the one reported in the hot-pressing case, with a lattice constant of 10.625 Å. The second pyrochlore phase had a lattice constant of 10.74 Å, and was possibly $LaTaO_4$."