

ELECTRON STRUCTURES AND OPTICAL REFLEXION
SPECTRA OF IRON COMPLEX CYANIDES

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The structures of iron complex cyanides involve cubic lattices with iron atoms arranged in the nodes but distributed also over the cubic interstices in the cases when are present in two different oxidation states(1)

The iron atoms in the lattice nodes, surrounded octahedrally by the six CN groups as ligands, are alternatively coordinating with N and C atoms. Due to this, they are in the weak and strong ligand field with high and low spin electron configuration, respectively (2).

In the experimental procedure the reflexion spectra of fine powdered crystalline samples against Zeiss etalon as a white standard were obtained with a Zeiss VSU-2P spectrophotometer.

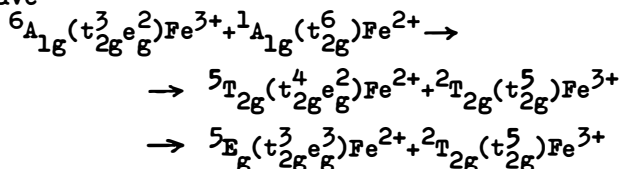
The data from recorded spectra are presented in Table

Table

Compound	Positions of observed bands ($\times 10^3 \text{cm}^{-1}$)
Prussian blue $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	17.4(vs), 25.5(s), 27.1(s)
Turnbull's blue $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$	17.5(vs), 25.35(s), 27.25(s)
oxidised $\text{Fe}_2[\text{Fe}(\text{CN})_6]$	16.5(vs), 25.0(s), 27.32(s)
vs=very strong s=strong	

The Prussian blue is by assumption the ferric ferrocyanide with the ground state ${}^6A_{1g}(t_{2g}^3 e_g^2)\text{Fe}^{3+} + {}^1A_{1g}(t_{2g}^6)\text{Fe}^{2+}$ where the Fe^{3+} and Fe^{2+} ions coordinate with N and C atoms, respectively.

Then, the 17400cm^{-1} transition observed can be a transfer of electron from Fe^{2+} to Fe^{3+} , both in the ground state. The next charge transfer is a one electron jump from Fe^{2+} to the excited state of Fe^{3+} ion. Thus, we have



and the difference between two final states is the excitation of an electron from t_{2g} to e_g orbital in the weak field ferrous ion. A good approximation of this is ${}^5T_{2g} \rightarrow {}^5E_g$ transition in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ion because the ligand field strength of the cyanide ion bonded through the nitrogen is comparable to that of H_2O (3). This transition is observed at ca 8000 and 10000cm^{-1} as was reported (4,5) and its doublet structure is due to Jahn-Teller effect or low symmetry component of ligand field lifting the degeneracy of the E_g state. According to this, the second charge transfer band should be expected at 25400 and 27400cm^{-1} which is in good agreement with observed spectrum of Prussian blue.

If the intensity of reflexion spectra can be used at all as a guide in assigning the bands the corresponding intensities of 17400 , 25400 and 27400cm^{-1} bands are in agreement with the fact that the last two transitions as "te" type should, by the argument of the local orthogonality be weak, compared with the first one of "tt" type.

The other assumption regarding Prussian blue as the ferrous ferricyanide is not confirmed because it gives the corresponding $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge transfer bands at ca 41000 and 48400cm^{-1} which fall in the region where no such bands are present concluding from the identical spectra in Robin's paper (2). This indicates that the first assumption is true and the Prussian blue is the

ferric ferrocyanide.

The d-d bands of Fe^{3+} high spin (4,5) and $[\text{Fe}(\text{CN})_6]^{4-}$ (6) are not observed probably due to the low intensity compared with the observed charge transfer processes.

The analogous interpretation is available for the spectra of Turnbull's blue (for many years it was thought to be the ferrous ferricyanide) and the oxidised $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ as they have the identical spectra.

As a consequence of this, it follows that in the case of the presence of iron ions in two different oxidation states the cation invariably has high spin and the anion a low spin electron configuration and that the latter appears preferably to form the low spin cyanoferrate (II). As indicated from the change of colour from white to dark blue $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ has undoubtedly undergone the oxidation and only the cation changes its valency state during this process. This is in agreement with the report (7) from Mössbauer spectra with these compounds as absorbers.

References

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