NOTES

1 : 10 Phenanthroline Complexes of Titanium(III) and Vanadium(IV)

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Chemical literature abounds with studies of metal complexes of phenanthroline. To cite a few, Clark¹⁾ studied complexes with $TiOCl_2$ and $VOCl_2$ and ascertained a ratio of 1 : 1 (metal : phen where phen=orthophenanthroline) for the two complexes; Herzog and Grimm²⁾ prepared $V(phen)_3$ and $V(phen)_3I_2$; Trujillo and Brito³⁾ determined the equilibrium constants of the vanadium (IV) phenanthroline complex to be 5.47 and 4.22, and Schaeffer⁴⁾ used the formation of a blue-coloured vanadium(II) phenanthroline complex as an end-point indicator in the titration of vanadyl compounds with chromium(II) chloride.

Orthophenanthroline forms light-slate-coloured and yellowish-white complexes with vanadyl sulphate and titanium(III) chloride respectively; these complexes are little mentioned in the existing chemical literature. These complexes were isolated, analysed, their magnetic susceptibilities measured, and their infrared spectra taken.

Experimental

Standard solutions of orthophenanthroline (E. Merck), vanadyl sulphate⁵⁾ (B. D. H.) and titanium(III) chloride (crystallized $TiCl_3 \cdot 6H_2O$)⁶⁾ were prepared in air-free, doubly-distilled water. Solutions of orthophenanthroline and metal salt were mixed in the molar ratio of 1 : 2 (metal : phen). The precipitates were then separated by centrifugation, washed repeatedly with tetrahydrofuran, dried in a vaccum desiccator over quick lime, and analysed.

Found: V, 14.03; SO_4, 25.9; C, 42.9; H, 3.16; N, 7.79%. Calcd for $VOSO_4$(phen): V, 14.85; SO_4, 27.99; C, 41.98; H, 2.33; N, 8.16%.

Found: Ti, 8.5; Cl, 19.45; C, 55.49; H, 4.33%; N, 10.7%. Calcd for $TiCl_3 \cdot (phen)_2$: Ti, 9.31; Cl, 20.7; C, 55.93; H, 3.11; N, 10.88%.

Both the complexes are water-soluble, but neither could be crystallised from its aqueous solution since both underwent hydrolysis. The densities of the vanadyl complex and the titanous complex are 1.639 g/cc and 1.368 g/cc respectively.

The $VOSO_4$(phen) complex is paramagnetic, with a molar susceptibility of 999.3×10^{-6}. The susceptibility of the complex after the correction for the diamagnetism of the ligand (128×10^{-6}) has been applied is 1.4 B. M. The titanium(III) complex is only slightly paramagnetic, having a corrected susceptibility of 0.3728 B. M.

The infrared spectra were taken in Nujol with a NaCl prism and in perfluorocarbon oil with a fluorotube in the appropriate ranges in order to obviate the spectral peaks of the solvents. (Figs. 1a and 1b). In the $TiCl_3(phen)_2$ complex, significant peaks were observed at 720, 780, 850, 890, 1140, 1185, 1375, 1425, 1450, 1550, 1600, 3100, and 3350 cm^{-1}. In the $VOSO_4$(phen) complex, important peaks were observed at 725, 855, 980, 1040, 1430, 1512, and 1660 cm^{-1}.

Discussion

The magnetic susceptibility of the vanadyl complex is 1.46 B. M. This may be considered to be a proof for the presence of a single unpaired electron in the vanadyl sulphate complex, although crystalline $VOSO_4 \cdot 5H_2O$ possesses a value of 1.73 B. M.⁷⁾ The low value cannot be explained. The titanous complex is only slightly paramagnetic, although a value of about 1.73 B. M. was expected. Probably the titanous in the complex is somewhat oxidised to titanic with ageing.

The out-of-plane H-deformation vibrations of free phenanthroline at 734 and 841 cm^{-1} are modified on coordination.

Phenanthroline	855, 841, 734	
$TiCl_3(phen)_2$	720, 780, 850, 890	1140, 1185
$VOSO_4$(phen)	725, 855, 980	
1040		
Assignment V=O	out-of-plane H-deformation vibrations	in-plane H-deformations or ring vibrations

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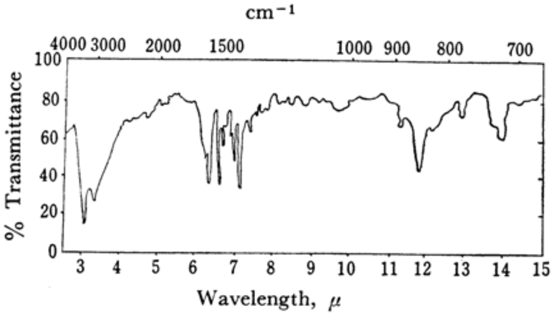

Fig. 1(a). $TiCl_3$ complex.

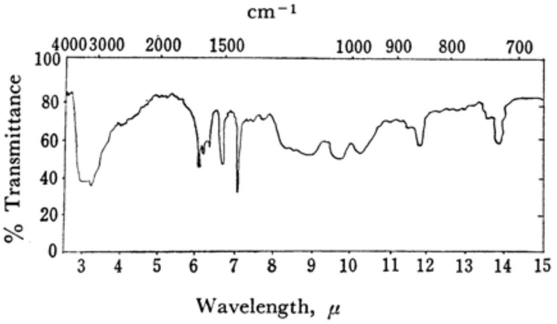

Fig. 1(b). $VOSO_4$ complex.

Clark1) has assigned the 868, 848, 734, and 718 cm^{-1} frequencies in $TiCl_4$(phen) and the 782, 845, 737, and 720 cm^{-1} frequencies in $VOCl_2$-(phen) to out-of-plane hydrogen-deformation vibrations. He has given the region from 300 to 380 cm^{-1} to M–Cl vibrations, which we did not study. Schilt and Taylor8) have mentioned the possibility that the bands in the orthophenanthroline complexes in the 1125—1250 cm^{-1} region may be due to in-plane hydrogen-deformation motions or to ring vibrations. The vanadium oxygen stretching frequency is located at 890 cm^{-1}(1) in $VOCl_2$(phen) and at 995 cm^{-1} in vanadyl acetylacetone9); therefore, we may presume it to be located at 1040 cm^{-1}, since at 980 cm^{-1} a feeble peak is observed in the case of phenanthroline also. The peaks in phenanthroline at 1423, 1505, and 1590 cm^{-1} are shifted to higher frequencies on coordination (in the titanous complex 1450, 1550, and 1600 cm^{-1}; in the vanadyl complex, 1430, 1512, and 1660 cm^{-1}), as has been observed by Schilt and Taylor8) in a large number of complexes of orthophenanthroline. It was also observed that there is quite a strong absorption peak at 3350 cm^{-1} in orthophenanthroline, a peak which is shifted to 3120 cm^{-1} in the vanadyl complex, whereas in the titanous complex the peak at this frequency becomes very strong and another peak appears at 3100 cm^{-1}. In view of the present data, it is not plausible to assign any frequency to the metal-nitrogen coordinate bond in orthophenanthroline.

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