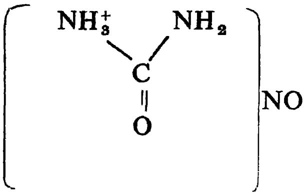
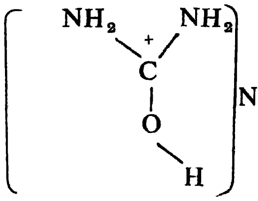
movement of labile H^+ ions from urea nitrate. On the basis of I.R. spectral data Davies and Hopkins[4] concluded that the point of proton attachment is the nitrogen (structure I). On the other hand, Redpath and Smith[5] on the basis of NMR studies favoured structure II, for urea nitrate



Structure I



Structure II

According to Kutty and Murthy[6] both the structures I & II exist in the solid state becasue of the strong hydrogen bonding net work in the solid with comparatively high mobility for the proton. This changes the electroneutrality of strontium carbonate and causes the displacement of Sr^{2+} ions which in turn combine with the nitrate present at the interphase resulting in the formation of strontium nitrate. These steps occurring at the phase boundary are followed by the bulk reaction, the rate of which varies depending upon the particle size of the reactants. The movement of nitrate ions from the bulk takes place due to the concentration gradient set up by the removal of nitrate ions at the surface.

The participation of water in this reaction as adsorbed or otherwise held at the surface is ruled out by the fact that the mixture forms a paste only at the later stage of grinding. To prove that the reaction takes place simply on grinding in the solid state, physical methods like infra-red spectrum and X-ray powder diffraction are adopted, where the solvent does not play any role at all. The work is being continued in this direction.

Strontium occurs in nature as strontianite. Therefore the method described here may be utilized to concentrate strontium content from the very low grade ore.

References

1. D. N. Pathak, *Proc. Nat. Acad. Sci.*, 1976, **46**(A) I, 73.
2. T. R. N. Kutty and A. R. V. Murthy, *Indian J. Tech.*, 1972, **10**, 305.
3. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis". 2nd Ed. Longmans Green & Co., London, 1958.
4. M. Davies and L. Hopkins, *Trans. Faraday Soc.*, 1957, **53**, 1563.
5. C. R Redpath and J. A. S. Smith, *Trans. Faraday Soc.*, 1962, **58**, 462.
6. T. R. N. Kutty and A. R. V. Murthy, *Indian J. Chem.*, 1973 **11**, 253.

Preparation and Characterisation of Some Pyridine Compounds of Cu(II) with Molybdate, Vanadate and Tungstate Anions

R. N. P. SINHA

Department of Chemistry, Ranchi University, Ranchi-8

and

G. P. SAHU

Department of Chemistry, St. Xavier's College, Ranchi

Manuscript received 12 September 1978, accepted 22 December 1978

THREE new compounds $Cu(VO_3)_2.Py.3H_2O$, $CuMoO_4.4Py.2H_2O$ and $CuWO_4.Py$ have been prepared and their I.R. spectra studied. Chemical literature of the last hundred years reveals practically no information on complexes of Cu(II) with pyridine having molybdate, vanadate and tungstate anions of the above mentioned compositions.

Experimental

Pure crystalline $CuSO_4.5H_2O$ (B.D.H. quality) was dissolved in minimum amount of water and to this pyridine (S. Merck) was added dropwise till the colour turned to intense blue. Thereafter, saturated solution of ammonium-metavanadate (A.R.) was added slowly with constant stirring until the precipitation was complete. The reaction mixture was digested on a water bath for nearly an hour, left overnight, filtered, washed with hot water containing a little of pyridine till free from vanadate, alcohol containing a few drops of pyridine and finally with ether. A-yellowish green product obtained was dried in a vacuum desiccator and analysed.

[Found : Cu.16% ; C, 15.52% ; H, 2.65% ; N, 3.45%, calcd. for $Cu(VO_3)_2.Py.3H_2O$: Cu, 16.10% ; C, 15.21% ; H, 2.78% ; N, 3.54%]. Exactly the same procedure was followed with ammonium molybdate (B.D.H.) and sodium tungstate (B.D.H.) solutions to get light blue and dark green substances respectively. The compounds were analysed. [Found : Cu, 10.87% ; C, 42.10% ; H, 4.05% ; N, 9.42%, calcd. for $Cu MoO_4.4Py.2H_2O$: Cu, 11.04% ; C, 41.70% ; H, 4.17% ; N. 9.73%] and [Found : Cu, 16.39% ; C, 16.20% ; H, 1.05% ; N, 3.16% ; calcd. for $Cu WO_4.Py$: Cu, 16.27% ; C, 15.36% ; H, 1.28% ; N, 3.58%].

The I.R. spectra were recorded on a grating infra-red spectrometer (Perkin and Elmer Model-337) at the C.D.R.I., Lucknow.

Discussion

Pyridine vibrations have been reported[1] to be in the region of 3000 cm^{-1} because of C – H mode and other vibrations at 1578, 1550, 1478, 1436, 1372, 1350, 1217, 1145, 1085, 1067, 1031, 991, 942, 886, 747, 700, 652, 605 and 405 cm^{-1}. There is a very broad band in the region of 3600 to 3000 cm^{-1}, region corresponding to H_2O and or C–H in the compounds. This indicates the presence of water molecule in coordinated and H-bonded form[2]. This also indicates the presence of pyridine molecules. The pyridine vibrations in the region of 1600 cm^{-1} to 400 cm^{-1} are very clear. However, some of the bands appear to have been mixed up due to the vibrational bands of the anions present in the compounds. Also, there are slight shiftings in the pyridine bands indicating coordination to metal ions. Similar shiftings have been found in many pyridine compounds by other workers[3]. Pyridine has a strong band at 750 cm^{-1} corresponding to out of plane C–H vibration[4]. This may be taken as an evidence for a weak bonding between pyridine and the metal ions in the compounds. There are medium bands also in the 1600 cm^{-1} region corresponding to H_2O mode of vibration. Aquo-complexes generally show vibrational band in this region[5]. The vibrational mode of coordinated water has been observed by several workers[6-8] in the region of 800 cm^{-1} and the band is very weak. The infra-red data of the compounds indicates the presence of a weak band in this region corresponding to coordinated water molecules. These bands are observed at 820 cm^{-1} and 830 cm^{-1} in the compounds. Strong infra-red bands at 920 and 895 cm^{-1} in the spectrum of $CuMoO_4.4Py.2H_2O$ may be due to MoO_4-mode. Similarly a doubt at 640 cm^{-1} and a weak band at 660 cm^{-1} in its spectrum may have a major contribution from MoO_4. The strong broad absorption at 790 cm^{-1} may also have contribution from MoO_4. On comparison of I.R. spectrum of this compound with that of $Cu(VO_3)_2.Py.3H_2O$, it appears that there is a new strong band at 820 cm^{-1} and very broad bands at 590 cm^{-1} and 525 cm^{-1}. As these bands[9] are present only in the spectrum of $Cu(VO_3)_2.Py.3H_2O$, they may be assigned to VO_3 group. The presence of a broad absorption hump in the region of 1000-700 cm^{-1} in the infra-red spectrum of $CuWO_4.Py$ may be due to WO_4 vibrations. Since there is no such absorption in the spectra of any of the other compounds mentioned here, it appears that this assignment is reasonable. There is a medium band in the region of 1600 cm^{-1} in the I.R. spectra of the compounds suggesting coordinated water molecule[5]. On this basis the compound may also be thought to be as $CuWO_4.Py.H_2O$ instead of $CuWO_4.Py$, as suggested on the basis of elemental analysis.

Acknowledgement

Thanks are due to Prof. H. C. Mishra for encouragements and extending possible laboratory facilities.

References

1. D. M. ADAMS, "Metal-Ligand and Related Vibrations", Ed. 1967, p. 306.
2. K. NAKANISHI, "Practical Infra-red Spectroscopy", Holden Dat. Inc., New York, Ed. 1964, p. 36.
3. D. M. ADAMS, "Metal-Ligand and Related Vibrations", Loc. cit.
4. CANON and SUTHERLAND, *Spectrochim Acta*, 1951, **4**, 373.
5. L. J. BELAMY, "The Infra-red Spectra of Complex Molecule", John Wiley and Sons Inc., 1956, p. 94.
6. I. GOMO, *Bull. Chem. Soc.*, Japan, 1961, **34**, 760.
7. G. SARTORI, C. FURLANI and A. DAMIANI, *J. Inorg. Nuclear Chem.*, 1958, **8**, 119.
8. I. NAKAGAWA and T. SHIMANOUCHI, *Spectrochim. Acta.*, 1964, **20**, 429.
9. L. J. BELAMY, "The Infra-red Spectra of Complex Molecules", John Wiley and Sons. Inc., 1956, p. 233.

Synthesis of Oxovanadium(IV) Complexes with Some New Tridentate Schiff Bases

A. SYAMAL*, K. S. KALE and S. BANERJEE†

Department of Applied Sciences and Humanities, Kurukshetra University, Kurukshetra 132 119, Haryana

and

Department of Chemistry, Regional Engineering College, Kurukshetra 132 119, Haryana

Manuscript received 17 March 1977, accepted 12 December 1978

THE metal complexes of tridentate dibasic ligands usually exhibit novel magnetic, spectral and structural properties[1-4]. The dibasic behaviour of these ligands forces the metal (II and III) ions to dimerise or polymerise leading to metal complexes with unusual magnetic properties. In recent years there has been considerable interest on the syntheses and magnetic properties of copper(II) and oxovanadium(IV) complexes of tridentate ONO donor dibasic Schiff bases derived from salicylaldehyde or substituted salicylaldehyde and orthoaminophenol[5-7]. In this preliminary communication we report the synthesis of several new oxovanadium(IV) complexes of Schiff bases derived from salicylaldehyde or substituted salicylaldehyde and orthoaminobenzylalcohol. It may be mentioned that this is the first report on the metal complexes of these ligands and we wish to make a comprehensive study of the coordination complexes of these ligands with various transition and non-transition metal ions.

General Method of Synthesis of the Complexes :

A methanolic solution (50 ml) of the appropriate ligand prepared *in situ* was reacted with a methanolic solution of freshly prepared oxovanadium(IV) acetate under reflux with stirring. The separated precipitates were filtered, washed with methanol and dried under vacuum. The analytical data of the complexes are presented in Table 1.

The absence of the ν(OH) stretch in the infra-red spectra of the complexes indicates the deprotonation of the ligands and dibasic character of these ligands. The $\nu(V=O)$ frequency of the complexes occurs at

---

* For correspondence

† Dept. of Chemistey, Institute of Science, Bombay-400032