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A Pentaaza Neutral Complex of Uranyl Ion: [2,6-Diacetylpyridine-bis(2′-pyridylhydrazonato)NNNNN] dioxouranium(VI)

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Examples of deprotonation of polyaza-ligands derived from pyridine-2-aldehyde-2′-pyridylhydrazone (PAPHY) coordinated to transition metal ions, which allow ionic complexes to be transformed into neutral complexes, are reported in the literature [1–9].

It has been shown that derivatives of PAPHY [2] and other ligands [3] containing the essential –N=C–NH–N=C–C=N– sequence of donors (capable by deprotonation of conversion to =N–C=N–N=C–C=N–) behave similarly.

We have utilized the 2,6-diacetylpyridine-bis(2′-pyridylhydrazone) (L) [10] for preparing the first pentaaza neutral complex, with diazinic sequences, of uranyl ion, containing uranyl–nitrogen covalent bonds.

Treatment of $UO_2(NO_3)_2 \cdot 6H_2O$ in AcOEt with L in different ratios and at different temperatures affords the same red product, which analyzes for $[(UO_2)_3L_2(NO_3)_{6-x}](NO_3)_x$ (I). ($C_{38}H_{38}N_{20}U_3O_{24}$ requires: C = 24.36, H = 2.03, N = 14.96, U = 38.14%; found C = 24.44, H = 2.00, N = 14.84, U = 37.90%).

The i.r. spectrum of (I) in KBr pellets shows significative bands at 3283 (m, ν_{N-H}, 1470 and 1285 (vs, consistent with coordinated nitrate groups), 1385 (s, typical of ionic nitrate groups) [11–15], 940 (vs, ν_{as} O=U=O), and bands characteristic of coordinated pyridine [6, 10] in the region 1620–1440 cm^{-1}.

The deprotonation of (I) is achieved by suspending (I) in anhydrous acetonitrile in the presence of an excess of 1,8-bis(dimethylamino)naphthalene (Proton sponge); a black product (II), stable in the solid state, is thus very easily and quantitatively obtained. ($C_{19}H_{17}N_7UO_2$ requires: C = 37.19, H = 2.77, N = 15.99, U = 38.82%; found: C = 37.55, H = 2.97, N = 15.83, U = 38.66%).

Compound (II) is not conducting in nitrobenzene solution and although the i.r. spectrum (KBr pellets and Nujol mull) is rather complex, there is no evidence for N–H and NO_3 stretching vibrations, while the ν_{as} O=U=O is lowered to 911 cm^{-1}. It is to point out that bis-protonated form of the ligand is easily recovered from both (I) and (II) when treated with dilute mineral acids, and L is slowly obtained by action of water on (II). This indicates that the ligand in (II) is only a deprotonated form of L.

Furthermore (II) reacts at room temperature with anhydrous methano giving a polymeric methoxylate uranyl complex of general formula $[L(UO_2)_2(OCH_3)_4CH_3OH]$ as shown from analytical data and spectroscopic measurements (found: C = 27.98, H = 3.38, N = 9.64, U = 45.98% $C_{24}H_{35}N_7U_2O_9$ requires: C = 27.66, H = 3.66, N = 9.41, U = 45.72%). I.r. data (KBr pellets): 3284(ms), 2811(m), 1611(s), 1579 (ms), 1564(m), 1528(m) 1458(ms), 1440(vs), 1375 (m), 1364(m), 1338(w), 1295(w), 1279(w), 1263(m) 1168(m), 1152(m), 1143(m), 1105(w), 1050(w) 1021(s), 1007(vs), 911(vs), 885(m), 847(w), 807(m), 782(w) 766(ms), 735(m), 643(w), 637(w), 548(w), 490(w), 422(m) 415(mbr) cm^{-1}). Further physicochemical characterization is in progress.

All these facts support the probable structure, reported in Figure 1, which is highly stabilized by the presence of the 5–5–5–5 chelation mode, which allows the highest resonance of the system.

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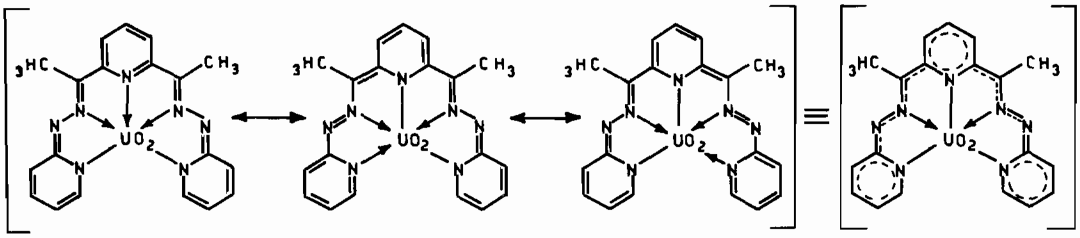

1 2 3 4

Figure 1. Equivalent resonance forms (1, 2, 3) in terms of the valence bond structure and delocalized electronic structure (4) of the complex(II).

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