et

$$(UO_2)_3(OH)_2\cdot aq^{4+} \longleftrightarrow (UO_2)_3(OH)_5\cdot aq^{+} + 3H^{+}.$$

L'alcalinisation ultérieure donne $(UO_2)_3(OH)_6\cdot aq$ et puis $(UO_2)_3(OH)_7\cdot aq^-$ à partir duquel précipite l'hexauranate $Na_2U_6O_{19}$.

Nous avons ensuite, utilisant une burette à gaz programmée [3], effectué une série de courbes de titrages potentiométriques de solutions de $UO_2(NO_3)_2$ (0.02 *M* à 0.1 *M*) par du Na_2CO_3 (1 *M*) sous une pression croissante ou constante (1 atm) de CO_2. Nous avons réalisé aussi une étude cinétique de l'absorption du CO_2 dans des suspensions aqueuses d'uranates de sodium. Les différents réseaux de courbes de titrages potentiométriques obtenues nous ont permis de déduire l'existence d'espèces carbonatées en solution. En milieu acide, les complexes carbonatés sont obtenus à partir des espèces hydroxylées:

$$(UO_2)_2(OH)_2^{2+} + H_2CO_3(\text{solution}) \rightleftarrows (UO_2)_2\,CO_3^{2+} + 2H_2O$$

$$(UO_2)_3(OH)_4^{2+} + 2H_2CO_3(\text{solution}) \rightleftarrows (UO_2)_3(CO_3)_2^{2+} + 4H_2O$$

$$2(UO_2)_3(OH)_5^{+} + 5H_2CO_3(\text{solution}) \rightleftarrows (UO_2)_6(CO_3)_5^{2+} + 10H_2O$$

$$2(UO_2)_3(OH)_6 + 6H_2CO_3(\text{solution}) \rightleftarrows (UO_2)_6(CO_3)_6 + 12H_2O$$

$$2(UO_2)_3(OH)_7^{-} + 7H_2CO_3(\text{solution}) \rightleftarrows (UO_2)_6(CO_3)_7^{2-} + 14H_2O$$

et à partir de la précipitation, il faut tenir compte des équilibres entre les phases précipitées et les espèces en solution, l'ensemble des réactions étant commandé par la moindre solubilité de $UO_2(OH)_2$. En milieu neutre et basique une seule espèce se forme: le tricarbonate d'uranyle et de sodium qui se présente sous forme dimère étant donné la forme des réseaux de courbes de titrage: $(UO_2)_2(CO_3)_6^{8-}$.

En milieux hydroxylé et carbonaté, les mêmes degrés d'isopolycondensation de l'ion UO_2^{2+} se rencontrent au cours de l'hydrolyse des sels d'uranyle.

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Equilibria in Acetone Medium. Binary Systems Involving Cobalt(II) Halides and Pyrazole-Derived Ligands

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Stability data associated with CoX_2–DMPPz binary systems (X = Cl^-, Br^-, I^-; DMPPz = 3,5-dimethyl-1-phenyl pyrazole) in anhydrous acetone, at 25.00 ± 0.05 °C, have been previously reported [1]. The present communication deals with equilibrium investigations – in the above mentioned solvent and temperature – on CoX_2–L binary systems, in which L = Pyrazole (Pz) and 3,5-dimethyl pyrazole (DMPz). It is clearly apparent from conductimetric and spectrophotometric measurements that the equilibria involved in these systems can be represented (without taking into account the solvation on the participant species), generically, by the equation: $CoX_2 + nL \rightleftarrows CoX_2L_n$, and the overall stability constants defined by: $\beta_n = [CoX_2L_n]/[CoX_2][L]^n$. The stability constants of the complex species were determined by combining the spectrophotometric method of corresponding solutions with the Fronaeus' computation technique [2]. The evaluated overall, as well as step (K_n) stability constants are (*system*, log β_n ± limit of error [2], log K_n): *$CoCl_2$–Pz*, $\log\beta_1 = 3.69 \pm 0.04$, $\log K_1 = 3.69$; $\log\beta_2 = 7.07 \pm 0.08$; $\log K_2 = 3.38$; $\log\beta_3 = 10.24 \pm 0.12$, $\log K_3 = 3.17$; $\log\beta_4 = 13.54 \pm 0.16$, $\log K_4 = 3.30$; *$CoBr_2$–Pz*, $\log\beta_1 = 4.54 \pm 0.05$, $\log K_1 = 4.54$; $\log\beta_2 = 8.76 \pm 0.10$, $\log K_2 = 4.22$; $\log\beta_3 = 12.85 \pm 0.15$, $\log K_3 = 4.09$; $\log\beta_4 = 16.90 \pm 0.20$, $\log K_4 = 4.05$; *CoI_2–Pz*: $\log\beta_1 = 4.00 \pm 0.04$, $\log K_1 = 4.00$; $\log\beta_2 = 7.69 \pm 0.09$, $\log K_2 = 3.69$; $\log\beta_3 = 11.22 \pm 0.13$, $\log K_3 = 3.53$; $\log\beta_4 = 14.79 \pm 0.18$, $\log K_4 = 3.57$; *$CoCl_2$–DMPz*: $\log\beta_1 = 4.53 \pm 0.05$, $\log K_1 = 4.53$; $\log\beta_2 = 8.78 \pm 0.10$, $\log K_2 = 4.25$; $\log\beta_3 = 12.69 \pm 0.15$, $\log K_3 = 3.91$; $\log\beta_4 = 17.02 \pm 0.20$, $\log K_4 = 4.33$; *$CoBr_2$–DMPz*: $\log\beta_1 = 5.22 \pm 0.06$, $\log K_1 = 5.22$; $\log\beta_2 = 10.13 \pm 0.12$, $\log K_2 = 4.91$; $\log\beta_3 = 14.83 \pm 0.17$, $\log K_3 = 4.70$; $\log\beta_4 = 19.71 \pm 0.23$, $\log K_4 = 4.88$; *CoI_2–DMPz*: $\log\beta_1 = 4.95 \pm 0.06$, $\log K_1 = 4.95$; $\log\beta_2 = 9.58 \pm 0.11$, $\log K_2 = 4.63$; $\log\beta_3 = 14.04 \pm 0.16$, $\log K_3 = 4.46$; $\log\beta_4 = 18.64 \pm 0.22$, $\log K_4 = 4.60$. A very good compatibility between the calculated formation constants and the pertinent experimental data was achieved for all the studied systems. The listed stability constants, in connection with previously determined values [1], indicate that in acetone medium and with *any* of the cobalt(II) halides as reference acceptor, the following basicity order holds: DMPz > Pz > DMPPz. Additional evidence in support of this sequence was also obtained from conductivity measurements . On the other hand, for each one of the ligands under consideration, the experimentally observed overall stability trend is: $CoBr_2L_n > CoI_2L_n > CoCl_2L_n$. It is perhaps worth noting that taking into account only the strength of the Lewis acids the expected stability order would be: $CoI_2L_n > CoBr_2L_n > CoCl_2L_n$. However, looking exclusively at the ionic radii of the halides the reverse order would be observed, owing to steric hindrance. The higher overall stabilities associated with the $CoBr_2L_n$ systems could be ascribed to a best compromise between the two aforementioned opposite effects. For the most part of these systems unusual stability patterns are found (*e.g.*, $K_4 > K_3$) suggesting possible changes in the mode of formation of the complex species as the number of coordinated ligands is increased [1, 3].

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Solvent and Ligand Interactions with the Ni(II) and Cu(II) Complexes of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane

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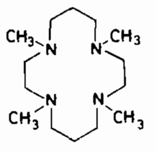
1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (L) forms metal complexes of different geometries at the metal ion and different configurations at the nitrogens [1].



L

Many of these complexes interact with solvent molecules or with ligands forming ternary species MLX^{2+} (eqn. 1)

$$ML^{2+} + X \overset{K_{MLX}}{\rightleftharpoons} MLX \qquad (1)$$

The Ni(II) complex with the *trans*-I (R,S,R,S) nitrogen configuration is especially interesting since it is tetra- or penta-coordinate. In poor donor solvent such as acetone square planar geometry is found, in water a mixture of the square planar and the penta-coordinate forms is found, whereas in DMF the penta-coordinate species predominates.

Addition of unidentate ligands such as SCN^-, OCN^-, N_3^-, F^-, I^-, OH^- and NH_3 to NiL^{2+} in any of the solvents mentioned gives mixed complexes with penta-coordinate geometry. The stability of these have been measured by spectrophotometric titrations with an on-line computer [2]. Similar experiments with CuL^{2+} in different solvents and with several ligands have also been carried out. All the Cu(II) complexes exhibit penta-coordination of the metal ion, thus being similar in this respect to the Ni(II) compounds.

The results indicate that the mixed complexes with the small and linear ligands such as SCN^-, OCN^- and N_3^- have the highest stabilities. Larger molecules such as pyridine and imidazole do not bind to the metal ion. This is a consequence of the steric interaction of the larger ligands with the four methyl groups of the macrocycle in its *trans*-I(R,S,R,S) configuration.

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Patterns in Lewis Acid–Base Interactions in Aqueous Solution

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The observable patterns in free energies of complex-formation in aqueous solution have lead to many