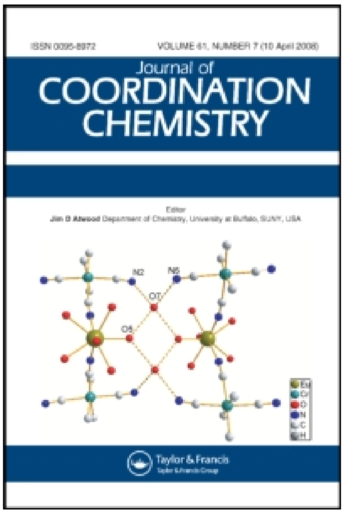

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NOTE

ACETYLACETONATOSELENITO COMPLEXES OF COBALT(II) AND NICKEL(II)

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Although mixed selenito complexes of Co(III) have been reported,[1−4] there have been no previous reports of selenito complexes of metals in the 2+ oxidation state. In the present paper we describe the preparation of the first mixed selenito complexes of Co(II) and Ni(II).

Keywords: Selenite, nickel(II), cobalt(II), complexes, synthesis.

RESULTS AND DISCUSSION

Mixed bis(2,4-pentanedionato)selenito complexes of Co(II) and Ni(II) of the general formula $M^I_2[M^{II}(C_5H_7O_2)_2SeO_3]\cdot nH_2O$, $M^I = Na^+$ or K^+, M^{II} = Co(II) or Ni(II) and n = 2 or 1 (for Na^+ and K^+ derivatives, respectively) were prepared by reacting $[M^{II}(C_5H_7O_2)_2(H_2O)_2]$, M^{II} = Co(II) or Ni(II), dissolved in organic solvents, with the stoichiometric amount of sodium or potassium selenite dissolved in the least amount of water. Generally, the amount of water in the reaction medium is a limiting factor in the preparation of the mixed selenito complexes. If the amount of water is kept to a minimum the mixed selenito complex is formed. Otherwise a normal selenite is obtained. This may be due to hydrolysis of the alkali metal selenite and the subsequent formation of an intermediate metal hydroxide complex. The resulting selenite anions can then substitute the hydroxy group possibly *via* a mechanism previously suggested by Stranks *et al.*[5]

The products are insoluble in all common solvents, a fact which suggests a polymeric structure for them. Attempts to prepare the corresponding ammonium, lithium and rubidium salts were unsuccessful.

Solid Na_2SeO_3[4] contains a free symmetrical SeO_3^{2-} ion of C_{3v} symmetry and as expected, two of the four vibrational modes are doubly degenerate. However, in normal selenites of the transition metals[6] three stretching and three bending vibrations of the SeO_3 group are observed which suggests that the degeneracy is lifted by virtue of the SeO_3 group acting as a bridge. This has been confirmed by single crystal X-ray studies of some transition metal selenites which have shown that C_s symmetry applies to the selenium atoms.[7−14]

In the mixed Co(II) and Ni(II) selenito complexes three stretching and two bending vibrations of the SeO_3 group are observed (See Table I) suggesting that these too are involved in a bridged structure similar to that found for normal selenites. The fact that

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TABLE I
Spectral and Magnetic Data for the Complexes.

Complex	Ir frequencies of the SeO_3 group (cm^{-1})		μ_{eff}(B.M.)	Electronic spectra (cm^{-1})		
	Stretching	Bending		ν_1	ν_2	ν_3
				$^4T_{1g} \rightarrow {}^4T_{2g}$	$^4T_{1g} \rightarrow {}^4T_{2g}$	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$
(1)	820m, br, 775 s, 740s, br, 655 m	500 m, 435 s	5.13	8930	15000	19200 20600
(2)	815 m, sh, 775 vs, br 720 m, sh, 655 m	495 m, br, 425, m	4.86	8930	14900	19200 20800
				$^3A_{2g} \rightarrow {}^3T_{2g}$	$^3A_{2g} \rightarrow {}^3T_{1g}$	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
(3)	820 m, sh, 775 vs, 740 vs, sh, 650 s	500 m, 440 s	3.31	9520 9900	16000	Obscured by charge-transfer bands
(4)	815 m, 790 s, sh, 770 s, br, 690 s, br 660 m, sh	520 s, 465 m, 430 m	3.43	9520 9900	14100 16300	

only two of the three bending modes are observed is not unusual since the low-frequency band is often of low intensity.[15]

The C–O stretching vibrations of the acetylacetonato ligands which occur at 1520–1527 and 925–936 cm^{-1} are not much effected by the replacement of coordinated water molecules by a selenite group in the products.

For an octahedrally symmetrical complex of Co(II) two well-characterised bands, one at high and one at low energy, together with one band of low intensity at medium energy appear in the electronic spectrum. The related Ni(II) compound generally gives rise to three absorption bands. The solid-state electronic transitions for the acetylacetonato selenito complexes of Co(II) and Ni(II) are given in Table 1. These are quite consistent with expectations. The magnetic moments of the complexes (Table I) are somewhat lower than the expected values for magnetically normal distorted octahedral complexes. The slight lowering of the values may be due to exchange between adjacent metal ions in the suggested polymeric structures.

The sizes of sodium and potassium cations are suitable for them to be incorporated in the lattice of these salts. However, lithium and rubidium ions appear to be too small or too large respectively to be accommodated in the structure. The complexes differ from those of Co(III) amine selenito compounds[4] which are soluble in water, and presumably do not have polymeric structures.

EXPERIMENTAL

Materials

Acetylacetone, nickel and cobalt chlorides, sodium selenite and other chemicals used were all of reagent grade.

Preparation of the starting complexes

The starting compound diaquo *bis*(2,4-pentanedionato)cobalt(II) was prepared from cobalt chloride hexahydrate and sodium acetylacetone.[16] The Ni(II) complex was prepared by a method similar to that used in the preparation of the manganese(II) complex.[17] Analysis for $[Co(C_5H_7O_2)_2(H_2O)_2]$: Calcd.: Co, 20.1; C, 41.2; H, 6.2 %. Found: Co, 21.0; C, 41.0; H, 6.0%. For $[Ni(C_5H_7O_2)_2(H_2O)_2]$: Calcd.: Ni, 20.0; C, 41.0; H, 6.2%. Found: Ni, 20.0; C, 40.0; H, 6.0%.

Sodium bis(2,4-pentanedionato) selenitocobaltate(II) dihydrate, (1)

A solution of 1.73g (10 mmol) of sodium selenite in the least amount of water was added gradually to a stirred solution of 2.93 g (10 mmol) diaquo bis(2,4-pentanedianato) cobalt (II) in 100 cm^3 hot chloroform. The addition was continued for one hour. A red rose precipitate was formed after a few minutes and its quantity increased continuously. The precipitate was recovered by filtration, washed with chloroform, then air-dried. The product was insoluble in all common solvents. Yield = 4.1 g (89%), m.p. > 220°C. Anal.: Calc. for $Na_2CoSeC_{10}H_{18}O_9$: Na, 9.9; Co, 12.6 Se, 16.9; C, 25.8; H, 3.9%. Found: Na, 8.4; Co, 13.0; Se, 16.2; C, 25.7; H, 4.0%.

Potassium bis(2,4-Pentanedionato)selenitocobaltate(II) monohydrate, (2)

The procedure adopted was the same as the previous one. 0.93g (4.5 mmol) of potassium selenite and 1.33 g (4.5 mmol) of the diaquo cobalt(II) complex were used. A rose red precipitate was formed. Yield = 1.84 g (84%), m.p. 250°C (decomp.) Anal.: Calc. for $K_2CoSeC_{10}H_{16}O_8$: K, 16.3; Co, 12.3; Se, 16.4; C, 25.0; H, 3.4%. Found: K, 16.8; Co, 12.6; Se, 16.9; C, 24.8; H, 3.4%.

Sodium bis(2,4-pentanedionato)selenitonickelate(II) dihydrate, (3)

1.73g (10 mmol) sodium selenite and 2.93g (10 mmol) of diaquo bis(2,4-pentanedionato) nickel(II) complex were used. The latter complex was dissolved in hot ethanol. A bluish green precipitate was formed. Yield=3.9 g(84%), m.p. > 220°C. Anal.: Calc. for $Na_2NiSeC_{10}H_{18}O_9$: Na, 9.9; Ni, 12.6; Se, 17.0; C, 25.8; H, 3.9%. Found: Na, 10.1; Ni, 12.4; Se, 17.8; C, 25.8; H, 3.9%.

Potassium bis(2,4-pentanedionato) selenitonickelate(II) monohydrate, (4)

The procedure followed was the same as the previous ones; 2.05g (10 mmol) of potassium selenite and 2.93g (10 mmol) of the diaquo nickel(II) complex were used. A green precipitate was formed. Yield=3.79g, (79%), m.p. 250°C (decomp.). Anal.: Calc. for $K_2NiSe\,C_{10}H_{16}O_8$: K, 16.3; Ni, 12.2; Se, 16.5; C, 25.0; H, 3.4%. Found: K, 16.1; Ni, 12.4; Se, 16.2; C, 25.5; H, 3.7%.

The alkali metal and ammonium selenites were prepared by reacting an aqueous solution of the corresponding chloride and a suspension of silver selenite.

The i.r. spectra in the range 4000–400 cm^{-1} were recorded on a Pye Unicam SP 1100 spectrophotometer, using KBr discs, and in the range 400–250 cm^{-1} in Nujol mulls between polyethylene plates on a Perkin-Elmer 598 spectrometer. Electronic spectra of the solids were recorded on a Beckman Acta MIV spectrophotometer provided with a diffuse reflectance attachment. Magnetic measurements were carried out at 20°C by the Gouy method.

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REFERENCES

1. H.L. Riley, *J. Chem. Soc.*, 2985 (1928).
2. P. Ray and A.N. Goch, *J. Indian Chem. Soc.*, **13**, 494 (1936).
3. C. Verhelyi, M. Somay and I. Kozma, *Studia Universitatis Babes, Bala; Chemia*, **19**, 66 (1974).
4. A.D. Fowless and D.R. Stranks, *J. Inorg. Chem.*, **16**, 1271 (1977).
5. *Ibid., idem.*, **16**, 1282 (1977).
6. K.A.R. Salib, S.B. El-Maraghy, S.L. Stefan and A.A. Emara, to be published.
7. M. Koskenlinna, L. Niinisto, and J. Valkonen, *Cryst. Struct. Comm.*, **5**, 663 (1976).
8. M. Koskenlinna and J. Valkonen, *Acta Chem. Scand.*, **A31**, 752 (1977).
9. V.G. Gattow, *Acta Cryst.*, **11**, 377 (1958).
10. J. Valkonen and M. Koskenlinna, *Acta Chem. Scand.*, **A32**, 603 (1978).
11. M. Koskenlinna and J. Valkonen, *Acta Chem. Scand.*, **A31**, 611 (1977).
12. B.O. Loopstra and N.P. Brandenburg, *Acta Cryst.*, **B34**, 1335 (1978).
13. M. Koskenlinna and J. Valkonen, *Acta Chem. Scand.*, **A31**, 638 (1977).
14. M. Koskenlinna and J. Valkonen, *Acta Chem. Scand.*, **A31**, 457 (1977).
15. K.A.R. Salib, R.A. Bucher, *Trans. Met. Chem.*, **8**, 360 (1983).
16. J. Ellern and R. Rogesdale, *Inorg. Synth.*, **11**, 82 (1968).
17. R.G. Charles, *Inorg. Synth.*, **6**, 164 (1960).