Tetracyano-Bis(triphenylphosphine) and -Bis(triphenylarsine)-Cobaltate(III) Complexes

Nobufumi Maki and Kanji Ohshima

Department of Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu

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Previously, we concluded that the disulfito- and diaquo-tetracyanocobaltate(III) complexes take a *trans*-configuration on the evidence of their polarographic behavior and absorption spectra.[1]

The present communication is concerned with the method of preparing and confirming two kinds of tetracyanocobaltate(III) complexes involving triphenylphosphine or triphenylarsine, $Na[Co(CN)_4(P{\equiv}\phi_3)_2]\cdot 3H_2O$ and $Na[Co(CN)_4(As{\equiv}\phi_3)_2]\cdot 3H_2O$ (a new complex),*1 from the *trans*-disulfito complex. The former was ascertained to be quite identical with that prepared by the method of Watanabe *et al.*[2]

The disulfito complex, $Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O$[3] (9.38 g), was suspended in 300 m*l* of glacial acetic acid containing 10.0 g of triphenylphosphine and refluxed at 75—80°C for six hours with stirring. The disulfito complex gradually dissolved into acetic acid.

The slurry residue, which was insoluble in acetic acid, was filtered off if it was yielded in the final stage of the reaction. The yellow filtrate was then diluted to 1200 m*l* by adding water and allowed to stand overnight under ice-cooling. The desired complex crystallized from the solution; it was filtered and washed with water, benzene, and ether to eliminate any excess ligands. Recrystallizations were made from an ethanolic solution by adding water. Found: Co, 7.67; C, 62.94; N, 7.38; H, 4.83%. Calcd for $Na[Co(CN)_4(P{\equiv}\phi_3)_2]\cdot 3H_2O$: Co, 7.71; C, 62.83; N, 7.33; H, 4.75%.

Analogously, the $Na[Co(CN)_4(As{\equiv}\phi_3)_2]\cdot 3HO_2$ complex was prepared as orange-yellow crystals by treating 11.66 g of $Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O$ with 14.52 g of triphenylarsine in 600 m*l* of acetic acid (100%) at 75°C for ten hours. Found: Co, 6.88; C, 56.42; N, 6.61; H, 4.30%. Calcd for $Na[Co(CN)_4(As{\equiv}\phi_3)_2]\cdot 3H_2O$: Co, 6.91; C, 56.36; N, 6.57; H, 4.26%.

Figure 1 shows the absorption spectra of tetracyanocobaltate(III) complexes in the visible and ultraviolet regions.

All the aspects of the polarographic behavior of the tetracyano complexes derived from the disulfito complex are very similar to each other; this suggests that their configurations are all *trans*-form. Table 1 summarizes the electrode processes and their half-wave potentials.

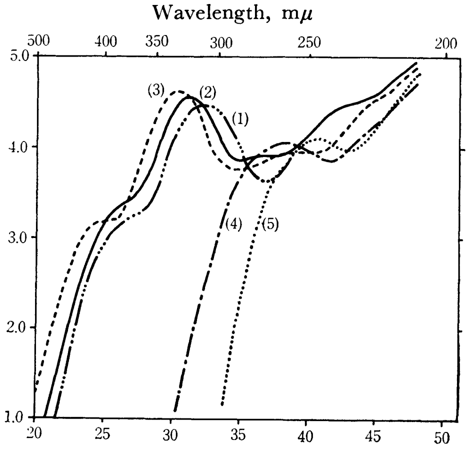

Fig. 1. The absorption spectra of the cobaltate(III) complexes in methanol solutions (25°C). (1) ------ *trans*-$Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O$; (2) —— $Na[Co(CN)_4(P{\equiv}\phi_3)_2]\cdot 3H_2O$; (3) ---- $Na[Co(CN)_4(As{\equiv}\phi_3)_2]\cdot 3H_2O$; —·—· (4) $P{\equiv}\phi_3$ in ethanol; (5) ······ $As{\equiv}\phi_3$ in ethanol.

Table 1. Half-wave potentials of the waves for tetracyanocobaltate(III) complexes (25°C)

Compound	1st wave	2nd wave	3rd wave
$Na[Co(CN)_4(P{\equiv}\phi_3)_2]\cdot 3H_2O$	−0.98 ($Co^{III} \rightarrow Co^{I}$)	−2.06 ($Na^{I} \rightarrow Na^{0}$)	
$Na[Co(CN)_4(As{\equiv}\phi_3)_2]\cdot 3H_2O$	−0.58 ($Co^{III} \rightarrow Co^{II}$)	−1.06 ($Co^{II} \rightarrow Co^{I}$)	−2.06 ($Na^{I} \rightarrow Na^{0}$)

DMSO solution containing 0.1 M $[(C_2H_5)_4N]ClO_4$ V *vs.* SCE

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[1] N. Maki and K. Yamamoto, This Bulletin, **43**, 2450 (1970).

[2] K. Watanabe, H. Nishikawa and M. Shibata, *ibid.*, **42**, 1150 (1969).

*1 ϕ=phenyl radical: C_6H_5-.

[3] H. H. Chen, M-S. Tsao, R. W. Gaver, P. H. Tewari and W. K. Wilmarth, *Inorg. Chem.*, **5**, 1913 (1966).