

ANILINE COMPLEXES OF CADMIUM(II) ACETATE*

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Although transition metal(II) halides, sulphates, and nitrates form complexes with nitrogen ligands, very few acetato complexes of these metals are known. This may be due to the fact that the donor ability of acetate is normally weaker than that of water, and it is only recently that the acetato complexes of some divalent metal ions have been described.¹⁻⁵ However, not much work seems to have been carried out on the spectroscopic studies of these complexes. The present communication describes the preparation and some spectroscopic studies on the complexes of cadmium(II) acetate with aniline, *ortho*-, *meta*-, and *para*-toluidines, and 3,4-xylydine.

The anilines were observed to form a range of complexes with cadmium(II) acetate. The purity of these complexes was checked by metal analysis (Table 1). The complex $2\text{Cd}(\text{OAc})_2 \cdot 3(m\text{-MeC}_6\text{H}_4\text{NH}_2)$ prepared has a non-integral ratio of the ligand molecules to the metal atom. This compound was obtained reproducibly in spite of varying the ratios of the reactants and must, therefore, be considered as a definite chemical entity.

Contributions due to the coordinated acetate group were selected by comparing the spectra of these complexes with cadmium(II) halide complexes of the corresponding ligand. The residual features were assigned to the coordinated acetate group and the frequencies are listed in Table 1. In some cases strong bands due to the acetate group features are believed to superimpose and mask some of the ligand bands.

Ideally, coordination by the acetate groups should be sought in their infrared spectra where it should be possible to distinguish ionic non-coordinated and co-ordinated species. The free acetate ion has a very low symmetry (C_{2v}) and has fifteen fundamental vibrations all of which are both infrared and Raman active.⁶ Of these, the infrared vibrations due to the COO^- group are: CO asymmetric stretch $\simeq 1580\text{ cm}^{-1}$; CO symmetric stretch $\simeq 1425\text{ cm}^{-1}$; CO_2 bending, CO_2 out-of-plane bending, and CO_2 rocking modes. It is well known that the acetate ion, like all the

* Manuscript received June 24, 1968.

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¹ Ablov, A., *C. r. hebd. Séanc. Acad. Sci., Paris*, 1934, **198**, 1789; *Bull. Soc. chim. Fr.*, 1936, [5] **3**, 1673.

² Semenenko, K. N., and Kurdyumov, G. M., *Vest. mosk. gos. Univ. (Ser. Mat., Mekh., Astron., Fiz., Khim.)*, 1958, **13**(2), 207 (*Chem. Abstr.*, 1959, **53**, 6866).

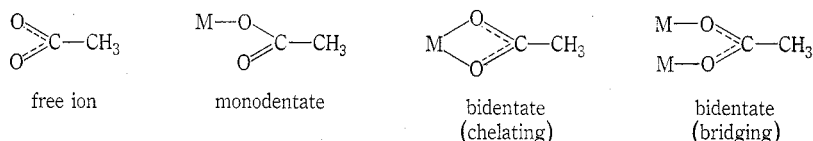
³ Kreshkov, A. P., Vil'borg, S. S., and Drozdov, V. A., *Trudj mosk. khim.-tekhrol. Inst.*, 1956, No. 22, 123 (*Chem. Abstr.*, 1957, **51**, 16193).

⁴ Tronov, B. V., and Kharitonova, R. I., *Izv. Akad. Nauk kirgiz. SSR*, 1955, **1**(6), 157.

⁵ Flint, C. D., and Goodgame, M., *J. chem. Soc. (A)*, 1967, 1718.

⁶ Nakamoto, K., Fujita, J., Tanaka, S., and Kobayashi, M., *J. Am. chem. Soc.*, 1957, **79**, 4904.

other oxyanions, coordinates to the metal through its oxygens. The anion may coordinate with the metal in one of the following ways:



On coordination the selection rule does not differ since all the modes are already infrared active in the free ion. The effect of coordination is usually judged from the separation of the CO asymmetric and symmetric stretching frequency shifts caused by complex formation.

TABLE I
ANALYTICAL DATA AND EXTRACTED INFRARED SPECTRA (cm^{-1}) OF CADMIUM(II) ACETATE COMPLEXES

Complex	Cd (%)		N-H Stretch		CO Stretch		Possibly M-O Mode
	Found	Calc.	Asym	Sym	Asym	Sym	
$\text{Cd}(\text{OAc})_2 \cdot \text{C}_6\text{H}_5\text{NH}_2$	34.6	34.2	3235	3130	1540	1400	247
$\text{Cd}(\text{OAc})_2 \cdot o\text{-MeC}_6\text{H}_4\text{NH}_2$	32.9	33.3	3225	3120	1540	1410	247
$2\text{Cd}(\text{OAc})_2 \cdot 3(m\text{-MeC}_6\text{H}_4\text{NH}_2)$	28.6	28.7	3240	3125	1539	1410	250
$\text{Cd}(\text{OAc})_2 \cdot p\text{-MeC}_6\text{H}_4\text{NH}_2$	33.1	33.3	3235	3120	1540	1413	250
$\text{Cd}(\text{OAc})_2 \cdot 2(3,4\text{-(Me)}_2\text{C}_6\text{H}_3\text{NH}_2)$	23.6	23.8	3248	3150	1552	1403	276

In addition to the ligand vibration modes, modified on account of coordination, two very strong bands were also observed in the regions and 1545 cm^{-1} 1405 cm^{-1} ($\pm 10 \text{ cm}^{-1}$) in the $2\text{--}15 \mu$ spectra of all the complexes. Since such bands were not observed in the spectra of the free ligands nor in the cadmium(II) halide-aniline complexes, it is considered that these bands are most probably due to the acetate group, that is, CO asymmetric and symmetric stretching modes respectively. Moreover, a strong band at $\approx 250 \text{ cm}^{-1}$ was also observed in the far-infrared spectrum of each of these complexes. Such bands in the low-frequency region have been assigned to metal-oxygen modes in the oxyanion complexes.^{5,7-10} It is thus clear that the acetate groups are coordinated in these complexes.

The shifts of the N-H stretching bands to lower frequencies are consistent with coordination of the amines.

Experimental

The complexes were prepared by heating cadmium(II) acetate with an excess of the appropriate ligand. The cadmium(II) acetate dissolved in the ligands and the complexes crystallized on cooling. The crystals were washed with ether.

⁷ Ferraro, J. R., and Walker, A., *J. chem. Phys.*, 1965, **42**, 1278.

⁸ Ahuja, I. S., Brown, D. H., Nuttall, R. H., and Sharp, D. W. A., *J. chem. Soc. (A)*, 1966, 938.

⁹ Ahuja, I. S., *Aust. J. Chem.*, 1968, **21**, 353.

¹⁰ Ahuja, I. S., *Inorg. chim. Acta*, in press.

Infrared spectra were recorded in the NaCl and KBr region as Nujol or hexachlorobutadiene mulls supported between sodium chloride plates using a Perkin-Elmer 125 spectrophotometer. The far-infrared spectra ($15\text{--}45\ \mu$) were recorded as Nujol mulls supported between thin polythene sheets on a Grubb-Parsons DM 2 spectrophotometer fitted with caesium iodide optics.

Acknowledgment

The author expresses his sincere thanks to the Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland, for the use of spectrophotometers.