Inorganica Chimica Acta, *211* (1993) 211–215

Spectroscopic study of cadmium(II) complexes with heterocyclic dithiocarbamate ligands

Soledad Garcia-Fontan and Pilar Rodriguez-Seoane
Departamento de Química Pura Y Aplicada, Universidad de Vigo, 36200 Vigo (Galicia) (Spain)

José S. Casas and José Sordo
Departamento de Química Inorgánica, Universidad de Santiago de Compostela, 15706 Santiago de Compostela (Galicia) (Spain)

Mark M. Jones
Department of Chemistry and Center in Molecular Toxicology, Vanderbilt University, Nashville, TN 37235 (USA)

(Received April 26, 1993)

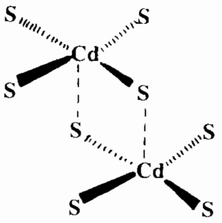
Abstract

Cadmium(II) dithiocarbamates [Cd(dtc)$_2$] (dtc = 4-carboxamidopiperidine-1-carbodithioate, morpholine-1-carbodithioate or 4-(2-hydroxyethyl)piperazine-1-carbodithioate) and [Cd(dtc)$_2$]·H$_2$O (dtc = 4-hydroxypiperidine-1-carbodithioate} have been prepared and characterized by thermal analysis and IR and NMR (^{13}C, ^{113}Cd) spectrometry. Two of these ligands have previously been shown capable of removing cadmium from its aged *in vivo* storage sites. The use of solid state ^{13}C NMR measurements to establish the coordination mode of the dithiocarbamate ligands is also examined and the difficulties which arise are discussed.

Introduction

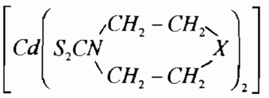
Interest in cadmium(II) dithiocarbamates [Cd(dtc)$_2$] has increased in recent years due to the potential utility of dithiocarbamate ligands as antidotes for chronic cadmium poisoning [1] and to the possible use of [Cd(dtc)$_2$] as single-molecule precursors for the deposition of II/IV semiconductor materials [2]. While a large number of dithiocarbamates have been shown capable of inducing the removal of cadmium from its storage sites *in vivo*, the chemistry of the products formed with cadmium is poorly characterized. These potential applications have prompted studies on the synthesis and coordination chemistry of these compounds in attempts to find correlations between their toxicological or technical properties and their structure.

Cadmium(II) dithiocarbamates are usually isolated as microcrystalline solids, which prevents X-ray diffraction measurements on monocrystals. As far as we know, the only members of this family for which crystal structures based on X-ray data have been reported are bis(diethyldithiocarbamato)cadmium(II) [3], bis(hexamethylenedithiocarbamato)cadmium(II) [4] and bis(dibutyldithiocarbamate)cadmium(II) [5], although the structures of the related compound bis(diethyldiselenocarbamato)cadmium(II) [6] and of anionic or neutral adducts of bis(dialkyldithiocarbamato)cadmium(II) [7] have also been described. The solid forms of all [Cd(dtc)$_2$] species studied so far [3–5] are composed of centrosymmetric dimers in which two of the four dithiocarbamate anions act as bridging ligands and the other two as terminal S,S-chelating ligands.



The scant X-ray diffraction data have been supplemented by spectroscopic measurements (mainly IR spectroscopy) in recent years. Techniques such as liquid and solid state ^{13}C and ^{113}Cd NMR spectroscopy, though barely explored, seem promising.

Here we report the synthesis and structural characterization, by IR and NMR (^{13}C and ^{113}Cd) spectroscopy, of some piperidine-, morpholine- and piperazine-based cadmium(II) dithiocarbamates with the general formula



$$\left[Cd\left(S_2CN\begin{matrix}CH_2-CH_2\\ \qquad\qquad X\\ CH_2-CH_2\end{matrix}\right)_2\right]$$

0020-1693/93/$6.00

where X = C(H)OH (in CdL$^1_2$, bis(4-hydroxypiperidine-1-carbodithioato)cadmium(II)), C(H)C(O)NH$_2$ (in CdL$^2_2$, bis(4-carboxamidopiperidine-1-carbodithioato)-cadmium(II)), O (in CdL$^3_2$, bis(morpholine-1-carbodithioato)cadmium(II)) or NCH$_2$CH$_2$OH (in CdL$^4_2$, bis[4-(2-hydroxyethyl)piperazine-1-carbodithioato] cadmium(II)). CdL$^1_2$ was isolated as its monohydrate.

In tests of their sodium salts [8], L^1 reduced acute Cd toxicity in mice when given 1–4 h after Cd and L^2 mobilized and promoted the excretion of metallothionein-bound metal; L^3 was less effective therapeutically. CdL$^3_2$ has been used for analytical purposes [9].

Experimental

Materials and instrumentation

The sodium salts of the dithiocarbamates L$^{1-3}$ were obtained as described [8]. NaL^4 was synthesized by a similar procedure from 1-(2-hydroxyethyl)piperazine. CdSO$_4$·8/3H$_2$O from a commercial source was used without further purification. Elemental analyses were carried out on a Perkin-Elmer 240 B microanalyser. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained simultaneously on a Mettler TA 3000 TG 50 thermobalance using a dynamic pure air furnace atmosphere (150 ml/min) and a heating rate of 20°/min. Sample weights ranged from 9.6 to 10.8 mg. Differential scanning calorimetry (DSC) curves were recorded on a Mettler TA 3000 DSC 20 system using *c.* 2 mg samples and a heating rate of 10°/min. IR spectra were obtained in KBr discs or Nujol mulls using a Perkin-Elmer 180 spectrometer. ^{13}C and ^{113}Cd NMR spectra in DMSO-d$_6$ solution were recorded at room temperature on a Bruker WM-250 spectrometer at 62.83 and 55.43 MHz, respectively. CP/MAS ^{13}C and ^{113}Cd spectroscopy was performed on a Bruker MSL-400 apparatus at 100.63 and 88.76 MHz, respectively; samples were packed in a 7 mm ZrO$_2$ rotor spinning at 4.0 kHz, and recycle times of 5.0 s (both nuclides), acquisition times of 20.0 (^{13}C) and 5.0 (^{113}Cd) ms and contact times of 1.0 (^{13}C) and 4.0 (^{113}Cd) ms were used.

Synthesis of complexes

Bis[4-(2-hydroxyethyl)piperazine-1-carbodithioato)]cadmium(II)

A solution of CdSO$_4$·8/3H$_2$O (0.85 g, 3.32 mmol) in water (60 ml) was added dropwise with stirring to a solution of sodium 4-(2-hydroxyethyl)piperazine-1-carbodithioato (2.00 g, 6.64 mmol) in methanol:water (80 ml, 1:1 vol./vol.). After 3 h, a solid formed that was collected by centrifugation, washed with water and dried in a dessicator over silica gel. The other complexes were isolated by similar procedures, using methanol–water ([CdL$^1_2$]) or water ([CdL$^2_2$] and [CdL$^3_2$]) as solvent. Note that, unlike previous work [8a], we obtained the monohydrated form of [CdL$^1_2$] and the non-hydrated form of [CdL$^2_2$] (Table 1).

Results and discussion

The compounds isolated are white or yellow solids (see Table 1). Their thermal behaviour is described in Table 2. The complexes [CdL$^1_2$]·H$_2$O and [CdL$^3_2$] underwent a single large mass change over a relatively narrow range of temperature (260–380 °C). In addition, the TG curve of [CdL$^1_2$]·H$_2$O shows the loss of crystallization water at *c.* 100 °C. Compounds [CdL$^2_2$] and [CdL$^4_2$] show a more complex decomposition pattern over a wider range of temperature (220–610 °C). The IR spectra of the final residues formed in the TG measurements show bands corresponding to the SO$_4^{2-}$ anion, indicating the presence of CdSO$_4$ (probably mixed with both cadmium oxide and cadmium sulfide).

The DSC curves of all the complexes show broad endothermic peaks coinciding with the beginning of the weight loss in the TG experiments. These broad peaks, together with their related energies (100–200 kJ/mol), indicate that the decomposition of the compounds is associated with their melting. In addition, the DSC curves of [CdL$^2_2$] and [CdL$^4_2$] show exothermic peaks at temperatures which are coincident with the inflexion points observed inside the decomposition range of the corresponding TG diagrams. These exothermic

TABLE 1. Analytical data[a] and physical characteristics for cadmium complexes

Compound	m.p. (°C)[b]	C (%)	H (%)	N (%)	Color
[CdL$^1_2$]·H$_2$O	264	29.7(29.8)	4.6(4.6)	5.0(5.0)	white
CdL$^2_2$]	300	32.3(32.4)	4.2(4.2)	10.7(10.8)	yellow
[CdL$^3_2$]	300	27.9(27.5)	6.7(6.4)	3.6(3.7)	white
[CdL$^4_2$]	230	32.1(32.4)	5.0(5.0)	10.6(10.7)	yellow

[a] Theoretical values in parentheses. [b] Melting points(DSC) occur with decomposition.

TABLE 2. TG/DTG data for the cadmium complexes

Compound	Weight loss range (°C)	DTG peak temperatures (°C)	Residue (%)
[CdL$^1_2$]·H$_2$O	260–350[a]	280	35.71
[CdL$^2_2$]	270–580	315; 420; 510; 555	28.51
[CdL$^3_2$]	320–380	370	36.18
[CdL$^4_2$]	220–610	250; 300; 510	28.10

[a] The weight loss corresponding to the loss of the water molecule was observed at approximately 100 °C.

peaks, which are not shown by $[CdL^1_2]\cdot H_2O$ and $[CdL^3_2]$, are possibly associated with the decomposition of the substituents at ring position four in L^2 and L^4.

Table 3 lists the most significant bands in the IR spectra of the ligands and complexes. In the 3500–3000 cm^{-1} region the hydrated sodium salts of the ligands show the very broad band typical of water; for ligands L^2 and L^3 this band is complicated by the presence of the additional –OH group, and for L^4 by the $-NH_2$ group. In the complexes (except for $[CdL^1_2]\cdot H_2O$) the water band disappears, leaving narrower bands due to the OH (L^3) and NH_2 (L^4, 3330s; 3180s) groups. The breadth and position of ν(OH) in the CdL^3_2 spectrum suggest hydrogen bonding [10], but in the spectrum of CdL^4_2 the breadth and position of ν(NH) show no hydrogen bonding and no coordination to the cadmium atom. The presence of water of crystallization in $[CdL^1_2]\cdot H_2O$ is confirmed not only by the ν(OH) band but also by the δ(HOH) band at 1640 cm^{-1} and the absence of the wagging, twisting and rocking modes in the ranges expected for coordinated water.

The C–N stretching vibration, which usually appears in dithiocarbamates as a strong band around 1500 cm^{-1}, has been identified in the spectrum of the sodium salts of the ligands as the strong band present around 1420 cm^{-1}. The position of this band is indicative of the degree of double bond character in the C–N bond ($\nu(C{=}N) = 1690\text{–}1640$; $\nu(C\text{–}N) = 1350\text{–}1250\ cm^{-1}$ [11]). In these ligands C–N has rather less double bond character than in dithiocarbamates with alkyl N-substituents [5, 10, 12], but the slight shift of ν(C–N) to higher wavenumbers upon complexation shows a slight increase in double bond character. The ν(C–S) band lies in the range 1010–960 cm^{-1} in the sodium salts of the ligands and practically does not shift upon complexation, showing that the degree of double bond character of the C–S bond does not change very much.

The presence of a single ν(C–N) band at higher wavenumbers than in the free ligand, together with a single band or two very close bands attributed to ν(C–S), is considered indicative of a bidentate or slightly anisobidentate dithiocarbamate [13–16]. Since the IR spectra of the complexes prepared in this work all show this pattern, we propose a coordination scheme based, as in other cadmium dithiocarbamates [5], on bidentate ligands. However, since the presence of ligand bridges based on weak interactions does not complicate the ν(C–N) or ν(C–S) region [5], the presence of such interactions cannot be ruled out. In the range 400–180 cm^{-1} there are slight shifts of the ligand bands, and shoulders under 300 cm^{-1} that might be due to ν(Cd–S) [10, 17].

TABLE 3. Most significant IR bands

Compound	ν(OH)	ν(CN)	ν(CS)
$NaL^1\cdot 2H_2O$	3400vs,b; 3200sh	1430s	960s
$[CdL^1_2]$	3460s; 3300s,b; 3200sh	1440s	960s
$NaL^2\cdot 5/2H_2O$	3400s,b	1425s	1010s
$[CdL^2_2]$		1445s	1010s, 990s
$NaL^3\cdot 2H_2O$	3400vs,b	1420s	985s
$[CdL^3_2]$		1440s	990s, 980s
$NaL^4\cdot 5/2H_2O$	3400s,b	1420s	990s
$[CdL^4_2]$	3420s,b	1435s	1000s, 990sh

s = strong, b = broad, sh = shoulder, vs = very strong.

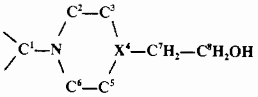
For CdL^4_2, interaction between the cadmium atom and potential donor groups other than S, i.e. NH_2 or C=O, can be ruled out because coordination causes no shift to lower frequencies of either ν(N–H) (already discussed) or ν(C=O) (1640 cm^{-1} in the sodium salt of the ligand, 1660 cm^{-1} in the complex).

Table 4 lists ^{13}C CP/MAS NMR data for the complexes. The C(1) signal is split in the $[CdL^1_2]$ and $[CdL^4_2]$ spectra. In the former, the signals of C(2,6) and C(3,5) are also split. This splitting of the C(1) signal also occurs in the spectrum of bis(dibutyldithiocarbamato)cadmium(II), which shows two signals at 204.7 and 199.3 ppm. In this compound, the splitting may be due to the presence of two different types of ligand: bridging and terminal S,S-chelating ligands [5]. Thus the spectral data for $[CdL^1_2]$ and $[CdL^4_2]$ are compatible with the dimeric coordination model observed in the dithiocarbamates studied by X-ray diffraction (see 'Introduction'), though other structures involving two magnetically non-equivalent C(1) atoms cannot be ruled out. In the remaining complexes the ligands are magnetically equivalent.

The coordination of the cadmium atom in one of the toxicologically more interesting complexes ($[CdL^2_2]$) was further explored using ^{113}Cd CP/MAS spectroscopy (Fig. 1). The isotropic chemical shift observed (Table 4) indicates that the cadmium(II) nuclide is much more shielded than in $[Cd(Et_2dtc)_2]$ [18]. Very similar isotropic chemical shifts have been observed for bis(pyrrolidinedithiocarbamato)cadmium(II) [18] and the sodium salt of bis(dimercaptomethylenemalononitrile)cadmium(II) [19]. Even though, in general, this parameter alone cannot unequivocally establish the nature of the cadmium coordination sphere [19], it is reasonable to treat it as more reliable when very similar ligands and complex stoichiometries are compared; on this basis, the value of δ_{iso} in Table 4 suggests that the structure of $[CdL^2_2]$ differs from those of the cadmium(II) dithiocarbamates that have been studied by X-ray diffraction [3–5]. However, this dissimilarity does not explain the greater efficacy of L^2 as antidote for acute Cd(II) poisoning because the chemical shift of $[CdL_2{}^2]$ in solution is similar to those of the other soluble complexes prepared in this work (Table 4) and to that of bis(diethyldithiocarbamato)cadmium(II) [20].

TABLE 4. ^{13}C and ^{113}Cd NMR data for the complexes

Compound	Conditions	C^1		C^2, C^6		C^3, C^5		C^4		C^7		C^8		δ ^{113}Cd ($W_{1/2}$)
		NaL	CdL_2	NaL	CdL_2	NaL	CdL_2	NaL	CdL_2	NaL	CdL_2	NaL	CdL_2	
$[CdL^1_2]\cdot H_2O$	DMSO-d_6	212.6	203.3	62.0	64.0	47.0	50.0	34.4	33.9					206.2[a] (281)
	CP/MAS		202.4 199.7		67.4 63.2		53.6 49.0		33.9					
$[CdL^2_2]$	DMSO-d_6	213.3	203.6	48.6	51.9	41.9	40.0	28.5	28.3	176.7	175.7			207.4[b] (210)
	CP/MAS		199.8		53.2		41.5		27.9		177.9			283.9
$[CdL^3_2]$	DMSO-d_6	214.4	205.4	66.1	65.6	49.7	52.1							
	CP/MAS		203.5		65.6		53.4							
$[CdL^4_2]$[c]	DMSO-d_6	213.9	204.3	53.3[d]	52.6[d]	49.0[d]	51.9[d]			58.4	58.4	60.1	59.5	200.0[e] (281)
	CP/MAS		201.4 199.0		53.4		53.4				59.9		59.9	



[a] In pyridine, $\delta = 222.9$ (99). [b] In pyridine, $\delta = 233.9$ (60). [c] The numbering scheme for L^1, L^2 and L^3 is similar. [d] Can be reversed. [e] In pyridine, $\delta = 220.7$ (131).

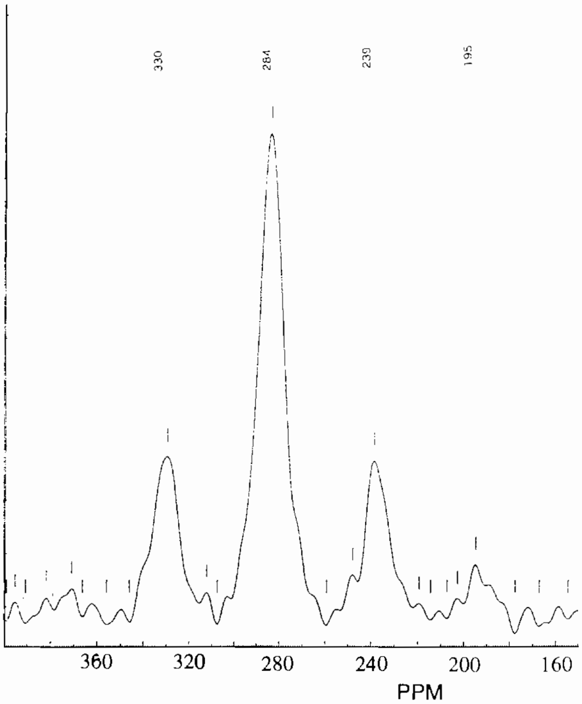


Fig. 1. CP/MAS ^{113}Cd NMR spectrum of $[CdL^2_2]$.

Note that the metal nuclide is further shielded in DMSO, probably because the oxygen atom of the solvent molecules is introduced into the coordination sphere to give the same S,O-coordination scheme for all dithiocarbamates. This hypothesis is supported by the chemical shifts values in pyridine being larger than in DMSO (Table 4) as is expected if the nitrogen donor atoms of the former solvent replace the oxygen atoms of the latter in the coordination sphere of the cadmium atom [21]. Note that the chemical shift of C(1) in DMSO-d_6 is greater than 200 ppm; this suggests that the ligands remain bidentate in this medium [22], ensuring coordination numbers greater than four for the cadmium(II) ion when the solvent contribution is included.

Acknowledgements

We thank the Comité Conjunto Hispano-Norteamericano para la Cooperación Científica y Técnica (Spain-USA) and the Xunta de Galicia (Spain) (XUGA81502188) for financial support; Drs J. Sanz and I. Sobrados and the National Solid State NMR Centre, Madrid, Spain, for the solid state spectra; and Professor A. Sánchez for helpful suggestions.

References

1 M.M. Jones and M.G. Cherian, *Toxicology, 62* (1990) 1.
2 M.B. Hursthouse, M.A. Malik, M. Motevalli and P. O'Brien, *Organometallics, 10* (1991) 730, and refs. therein.
3 A. Domenicano, L. Torelli, A. Vaciago and L. Zambonelli, *J. Chem. Soc. A*, (1968) 1351.
4 V.M. Agre and E.A. Shugam, *Sov. Phys. – Crystallogr., 17* (1972) 256.
5 J.S. Casas, A. Sánchez, J. Bravo, S. García-Fontán, E.E. Castellano and M.M. Jones, *Inorg. Chim. Acta, 158* (1989) 119.
6 M.B. Hursthouse, M.A. Malik, M. Motevalli and P. O'Brien, *Polyhedron, 11* (1992) 45.
7 R. Baggio, A. Frigerio, E.B. Halac, D. Vega and M. Perec, *J. Chem. Soc., Dalton Trans.*, (1992) 549, and refs. therein.

8 (a) G.R. Gale, L.M. Atkins, A.B. Smith, E.M. Walker, Jr., M.M. Jones and R.P. Hodge, *Res. Commun. Chem. Pathol. Pharmacol., 43* (1984) 281; (b) S.G. Jones, M.M. Jones, M.A. Basinger, L.T. Burka and L.A. Shinobu, *Res. Commun. Chem. Pathol. Pharmacol., 40* (1983) 155.

9 A.B. Sakla, A.A. Helmy, W. Beyer and F.E. Harhash, *Talanta, 26* (1979) 519; S. Soundararajan and M. Subbaiyan, *Indian J. Chem., 22A* (1983) 402; M.L. Riekkola, *Acta Chem. Scand., Ser. A, 37* (1983) 691.

10 A. Pagés, J.S. Casas, A. Sánchez, J. Sordo, J. Bravo and M. Gayoso, *J. Inorg. Biochem., 25* (1985) 35.

11 A.C. Fabretti, F. Forghieri, A. Giusti, C. Preti and G. Tosi, *Spectrochim. Acta, Part A, 40* (1984) 343.

12 J.S. Casas, M.V. Castaño, C. Freire, A. Sánchez, J. Sordo, E.E. Castellano and J. Zukerman-Schpector, *Inorg. Chim. Acta,* in press.

13 C.P. Sharma, N. Kumar, M.C. Khanopal, S. Chandra and Y.G. Bhide, *J. Inorg. Nucl. Chem., 43* (1981) 923.

14 C. O'Connor, J.D. Gilbert and G. Wilkinson, *J. Chem. Soc., 1* (1969) 84.

15 C. Petri, G. Tosi and P. Zannini, *J. Mol. Struct., 65* (1983) 283.

16 F. Bonati and R. Ugo, *J. Organomet. Chem., 10* (1967) 257.

17 A. Frigerio, B. Halac and M. Perec, *Inorg. Chim. Acta, 164* (1989) 149.

18 O.F.Z. Khan and P. O'Brien, *Polyhedron, 10* (1991) 325.

19 H.Y. Li and E.L. Amma, *Inorg. Chim. Acta, 177* (1990) 5.

20 R.A. Haberkorn, L. Que, Jr., W.O. Gillum, R.H. Holm, C.S. Liu and R.C. Lord, *Inorg. Chem., 15* (1976) 2408.

21 N.G. Charles, E.A.H. Griffith, P.F. Rodesiler and E.L. Amma, *Inorg. Chem., 22* (1983) 2717.

22 H.L.M. van Goel, J.W. Diesvel, F.W. Pijpers and J.G.M. van der Linden, *Inorg. Chem., 18* (1979) 3251.