Cobalt(II) and Zinc(II) Complexes of 1,1,5,5-Tetramethylcarbohydrazide

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1,1,5,5-Tetramethylcarbohydrazide ($Me_2NNH)_2$-CO(tmc) was synthesized via *the thermal decomposition of the carbamate $Me_2NNHC(O)OSiMe_3$. The complexes $Co(tmc)Cl_2$(III), $Co(tmc)_2Cl_2$(IV), $Zn(tmc)Cl_2$(V) and $Zn(tmc)_2Cl_2$(VI) were prepared. These compounds are non-electrolytes in solution in acetone and nitromethane. The complexes III and V have pseudo tetrahedral structures in the solid state and in solution in acetone, in which they are monomeric. The most likely solid state structure for the $M(tmc)_2Cl_2$ complexes IV and VI is octahedral. In solution, however, complexes IV and VI are extensively dissociated, via loss of one tmc ligand, giving equilibrium mixtures containing the four-coordinate complexes III and V, respectively. In all four complexes, the tmc ligand chelates to the metal centre* via *the carbonyl oxygen and one of the terminal dimethylamino groups. The ligand in $Zn(tmc)Cl_2$ is non-fluxional. Exchange among tmc ligands in solutions of $Zn(tmc)_2Cl_2$(VI) is rapid on the nmr time scale at temperatures above 0 °C.*

Introduction

Biological activity [1–7] associated with certain hydrazide compounds has prompted numerous studies of the coordination properties of N-acylhydrazines [4, 8–12], semicarbazides [13–19] and carbohydrazides [13, 14, 16, 20–26]. Thus, monodentate [2, 9, 11, 12, 14, 19] and bidentate [2, 4, 8, 13, 15, 16, 20–26] behaviour toward metal ions are reported for $XC(E)NHNH_2$ ligands (X = alkyl, aryl, amino, hydrazino; E = O, S) in tetrahedral [21, 24], square planar [18, 23], square pyramidal [22] and octahedral [8, 10, 16, 17, 21, 25, 26] structures. A common feature of many of the chelate complexes of $XC(E)NHNH_2$ is enolisation and deprotonation of the ligand, resulting in the formation of neutral complexes of the metal ion [1, 8, 12].

We report here a new and efficient synthesis of 1,1,5,5-tetramethylcarbohydrazide, together with studies of the solution, spectroscopic and magnetic properties of the Co(II) and Zn(II) complexes of this ligand.

Discussion

Several authors [27–29] have described the syntheses of 1,1,5,5-tetramethylcarbohydrazide (tmc). We found that a modification of the method of Wadsworth and Emmons [27], involving the reaction of phosgene, dimethylhydrazine and triethylamine in THF, gave high yields of tmc. In addition, we have found that the carbamate $Me_2NNHC(O)OSiMe_3$ I, obtained *via* the action of CO_2 upon $Me_2NNHSiMe_3$ [30], is decomposed quantitatively at 170–180 °C into tmc, hexamethyldisiloxane and CO_2 [31]. A plausible sequence of reactions is shown in eqns. 1 and 2.

$$2Me_2NNHC(O)OSiMe_3(I) \rightarrow Me_2NN(SiMe_3)C(O)OSiMe_3(II) + Me_2NNH_2 + CO_2 \quad (1)$$

$$Me_2NNH_2 + Me_2NNHC(O)OSiMe_3 \rightarrow (Me_2NNH)_2CO(tmc) + \tfrac{1}{2}(Me_3Si)_2O + \tfrac{1}{2}H_2O \quad (2)$$

Under mild conditions of pyrolysis (100 °C), compound I gives a quantitative yield of II, dimethylhydrazine, and CO_2. At higher temperatures, II is not observed, presumably on account of solvolysis by Me_2NNH_2 or H_2O.

The trimethylgermyl compound $Me_2NNHC(O)OGeMe_3$ also undergoes thermal decomposition in two stages, in the same way as I, but under milder conditions [31].

Tmc is a relatively high melting white solid, being insoluble in ether or hexane, and soluble in acetone, acetonitrile and THF. It is transparent in the UV/visible region characteristic of ligand field spectra of transition metal complexes. The n → π^* transitions of the carbohydrazide chain occur in the far ultra-

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violet [32] and reflect the amide–imidal tautomerism [33].

The infrared spectra of tmc as solid (KBr disc) or in solution (acetone) contain at least three bands due to ν(N–H), two bands in the amide I region, and a broad, poorly resolved band in the amide II region (Table II). Peak positions are dependent upon the medium, as expected for H-bonded systems. The assignments are based upon comparisons with literature data on related systems [4, 8, 9, 26, 34, 35]. The bands in the ν(N–H) region may arise because of hydrogen bonding effects and different orientations of the Me_2NNH groups about the carbonyl moiety, as observed in the crystal structure of $(H_2NNH)_2CO$ [36] and $(H_2NNH)_2CS$ [37]. The splitting of the amide I band of tmc is also attributable to this asymmetry of the coupled carbonyl–hydrazide groupings. The amide I and amide II bands are due primarily to C=O stretching and N–H bending motions, respectively [38, 39].

The ^1H NMR spectrum of tmc in acetone-d_6 and in $CDCl_3$ consisted of a single sharp methyl resonance and a single N–H resonance, at room temperature. As the temperature was lowered ($CDCl_3$ solution), the two resonances showed differential broadening. The N–H resonance became a doublet at –20 °C, while resolution of the CH_3 resonance into equal intensity peaks occurred at –26.5 °C. These observations are consistent with the existence of rotamers arising from restricted rotation about the (O)C–N bonds. The ^{13}C spectrum of tmc, in THF/acetone (4:1), consisted of singlets for the methyl and carbonyl carbons, at 47.60 and 157.6 ppm, respectively, in a 4:1 intensity ratio.

In principle, there are two modes of monodentate behaviour for tmc, involving either the carbonyl oxygen or one of the terminal dimethylamino nitrogen atoms. The amidic nitrogens (2 and 4, Fig. 1A) may be discounted on account of much lower relative basicity [13]. Chelation by tmc in the carbonyl form may give rise to a six-membered metallocycle, *via* the 1,5-nitrogen atoms (Fig. 1B), as has been claimed for carbohydrazide itself [13, 20]. Two kinds of five-membered metallocycle are possible, involving one of the terminal nitrogens and either the carbonyl oxygen (Fig. 1C), or the amide nitrogen atom (Fig. 1D). The five-membered ring structure 1C (O=S) is common among thiocarbazide complexes [16, 21–26]. Then, deprotonation of ‘C’ and ‘D’ is potentially capable of yielding the structures ‘E’ and ‘F’ (Fig. 1), in which the ligand would be anionic.

The complexes $Co(tmc)Cl_2$(III), $Co(tmc)_2Cl_2$(IV), $Zn(tmc)Cl_2$(V) and $Zn(tmc)_2Cl_2$(VI) were obtained *via* the solution reaction of the anhydrous metal chloride with the appropriate proportion of tmc. Analytical data, melting points and colours of the complexes are given in Table I, solution molecular weights, conductivity, magnetic moments, electronic spectra and NMR data in the Experimental section, and infrared data in Table II.

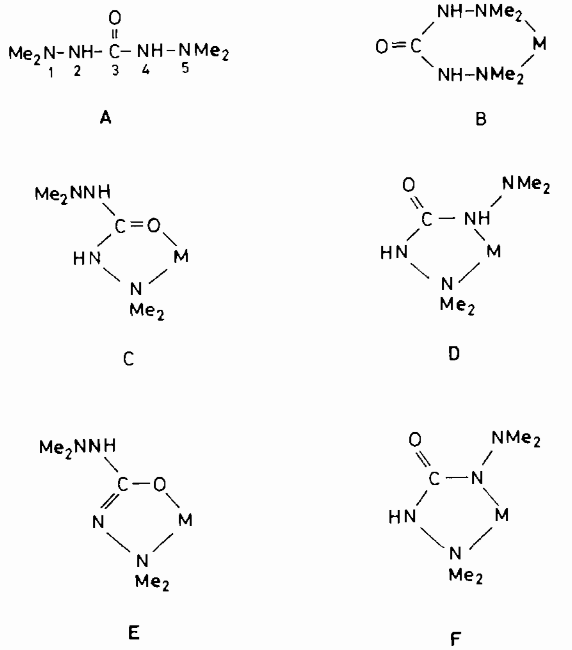

Fig. 1. Possible modes of chelation for tetramethylcarbohydrazide.

Cobalt(II) Complexes

The blue complex $Co(tmc)Cl_2$(III) was soluble in acetone and nitromethane, in which its conductivity (Λ_M = 25.7 and 19.9 l Ω^{-1} M^{-1}, respectively) was typical of a non-electrolyte [40]. The molecular weight of III in solution, in acetone, indicated a monomeric, undissociated species. The solid state (nujol mull) and the solution (acetone) electronic spectra of III were quite similar, showing an intense, highly structured band in the 15,000–20,000 cm^{-1} region, attributable to the ν_3 ($^4A_2 \rightarrow {}^4T_1(P)$) transition, and a much weaker band at 6700 cm^{-1}, due to the ν_2 ($^4A_2 \rightarrow {}^4T_1(F)$)) transition of pseudo tetrahedral Co(II) [41–48]. The ligand field splitting (10 Dq = 3790 cm^{-1}) and the electronic repulsion term (B = 690) were estimated, according to Lever [49], from the plots $\bar{\nu}_3/\bar{\nu}_2$ *versus* D_q/B and E($\bar{\nu}_3$)/B. The value of the magnetic moment of III (4.9 B.M.), however, is somewhat higher than is typical for pseudo tetrahedral structures.

The violet complex $Co(tmc)_2Cl_2$ (IV) was less soluble than III. It was a non-electrolyte in acetone and nitromethane (Λ_M = 13.1 and 27.7 l Ω^{-1} M^{-1}, respectively). The molecular weight of IV in acetone (M_{obs} = 396, M_{calcd} = 422) indicated dissociation, presumably into complex III and free tmc. In fact, the electronic spectrum of IV in acetone was very

TABLE I. Complexes of Co(II) and Zn(II) with $(Me_2NNH)_2CO$ (tmc).

		M.p. (°C)[a]	Analysis					
			Observed			Calculated		
			C	H	N	C	H	N
	tmc white	155–6	40.8	9.7	38.7	41.10	9.59	38.36
III	$Co(tmc)Cl_2$[b] blue	244–9	22.4	5.0	20.1	21.75	5.07	20.30
IV	$Co(tmc)_2Cl_2$[c] violet	234–6	28.6	6.7	26.5	28.44	6.64	26.55
V	$Zn(tmc)Cl_2$[d] white	202–6	21.2	5.10	19.4	21.25	4.96	19.83
VI	$Zn(tmc)_2Cl_2$[e] white	138–45	28.0	6.72	26.3	28.01	6.54	26.14

[a] All of the metal complexes melted with decomposition. [b] Soluble in acetone, acetonitrile. Insoluble in ether, THF. [c] See [b]. Also slightly soluble in chloroform, carbon tetrachloride. [d] Soluble in acetone, THF. Insoluble in ether, hexane, chloroform, carbon tetrachloride. [e] Soluble in acetone. Insoluble in ether, hexane.

similar to that of III, but with low intensity additional bands attributable to equilibrium concentrations of other 5- or 6-coordinated Co(II) species. Thus, the colour of the solution was violet, compared to the pure blue of compound III. The zinc complex, $Zn(tmc)_2Cl_2$, also dissociates in solution in a similar way to give $Zn(tmc)Cl_2$ and free tmc (*vide infra*). The solid state (nujol mull) electronic spectra of IV differ markedly from the solution spectra, showing low intensity bands in the regions typical for octahedral Co(II), as found in polymeric, chloro-bridged octahedral Co(II) systems [50]. The value of the magnetic moment obtained for complex VI is consistent for octahedral Co(II) [41, 43].

Zinc Complexes

The complex $Zn(tmc)Cl_2$ (V) is relatively soluble in acetone and THF. It is a non-electrolyte in acetone and nitromethane ($\Lambda_M = 6.8, 7.5\ l\ \Omega^{-1}\ M^{-1}$) and it is monomeric in acetone. The ^1H NMR spectrum of V in acetone-d_6 showed four resonances, corresponding to free and chelated Me_2NNH fragments of the tmc ligand (Fig. 1C). The ^1H resonance of the free dimethylamino moiety has essentially the same chemical shift as the Me_2N protons of the ligand itself. All other ^1H resonances in V are shifted downfield, relative to corresponding resonances for the ligand. The ^{13}C NMR spectrum of V consisted of two sets of narrow doublets for the free (47.47, 47.52 ppm) and the coordinated (50.52, 50.43 ppm) Me_2N groups and a single resonance for the carbonyl group (160.6 ppm). The coordinated centres showed significant downfield shifts relative to the corresponding ^{13}C resonances of the free ligand.

The complex $Zn(tmc)_2Cl_2$(VI) was soluble in acetone. It is a non-electrolyte in acetone and nitromethane ($\Lambda_M = 7.5, 21.5\ l\ \Omega^{-1}\ M^{-1}$). The low molecular weight observed for VI in acetone ($M_{obs} = 273$, $M_{calc} = 428.8$) indicated dissociation. The ^1H NMR spectrum of VI in deuteroacetone showed a single CH_3 resonance and a single NH resonance at room temperature. A similar spectrum was obtained when excess tmc was present. Thus, exchange among the free and the coordinated tmc ligands was rapid on the NMR time scale. At 0 °C, however, a solution of VI showed two resonances for the N–H protons, one corresponding to the $\overline{M-N-NH-C-O}$ metallocyclic unit and the other to the uncoordinated Me_2NNH fragment. The methyl resonance split into a doublet at –15 °C and into four equal intensity peaks at –50 °C. The ^{13}C NMR spectrum showed singlet resonances at room temperature for the C=O and CH_3 groups, again indicating rapid exchange.

Infrared Spectra

Solution IR spectra of tmc and its complexes III–VI were strongly solvent-dependent. For consistency, comparisons of solid phase (KBr pellet) spectra are described. In the ν(N–H) region, several bands and/or shoulders were observed for tmc and for complexes III–VI. The main N–H band for tmc was at 3180 cm^{-1}, a low value indicative of hydrogen bonding effects. For $M(tmc)Cl_2$ (III and V), two poorly resolved major ν(N–H) bands were observed, at 3290–5 and 3200–20 cm^{-1}, attributable to the N–H of the uncoordinated Me_2NNH group and to the ring N–H of the metallocycle, respectively (see Fig. 1C). Again, hydrogen bonding effects are indicated. For the $M(tmc)_2Cl_2$ complexes IV and VI,

TABLE II. Infrared Absorptions in the 3500–1500 cm^{-1} Region for $(Me_2NNH)_2CO$(tmc) Complexes of Co(II) and Zn(II).[a,b]

	ν(N–H)	Amide I	Amide II
I tmc[c]	3400(br,sh) 3280(m) 3180(s) 3090(sh)	1700(s) 1665(m)	1495(m)
IV Co(tmc)Cl_2	3300(s) 3210(vs) 3110(w)	1520(vs)	1550(s)
V Co$(tmc)_2Cl_2$	3280(sh) 3240(vs) 3120(w)	1630(vs)	1550(s)
Zn(tmc)Cl_2	3400(w,br) 3290(s) 3210(vs) 3090(w)	1630(vs)	1550(s)
Zn$(tmc)_2Cl_2$	3430(w,br) 3270(sh) 3240(vs)	1640(vs)	1550(s)

[a] Measured in KBr discs, in cm^{-1}. [b] Vs, s, m, w, sh, vb, b = very strong, strong, medium, weak, shoulder, very broad, broad. [c] In acetone, the ν(N–H) bands occurred at 3300(s), 3290(vs), 3200(sh), 3100(sh).

very broad, relatively intense absorptions at 3220 and 3240 cm^{-1} were observed. In all four complexes and in tmc, a weak, broad ν(N–H) absorption at ≈3400 cm^{-1} was present. Three ν(N–H) bands were also observed for tmc complexes of Ni(II) and Hg(II) [51].

The amide I band [38, 39] for tmc consists of two broad, overlapping absorptions at 1700 and 1660 cm^{-1}. The amide II band occurs at 1495 cm^{-1} and is overlapped by deformations due to the CH_3 groups. In the complexes III–VI, the amide I band is redshifted and occurs at 1620–40 cm^{-1} as a single broad resonance, while the amide II band is blue-shifted to 1550 cm^{-1}. Thus, the tmc ligands are coordinated in the same way in all four complexes, in a chelating fashion via the carbonyl oxygen and one of the terminal Me_2N groups.

Conclusions

Taken together, our physical data indicate that Co(tmc)Cl_2(III) has pseudo tetrahedral geometry in the solid state, while IV is octahedral. Octahedral Co$(tmc)_2Cl_2$(IV) could adopt four mononuclear isomeric arrangements, as well as several bridged possibilities. In solution, complex III is tetrahedral and IV is significantly dissociated into III and free tmc.

The Zn(tmc)Cl_2 complex V is a covalent, pseudo tetrahedral species in which tmc chelates to the metal via the carbonyl oxygen and a terminal Me_2N moiety of the ligand. A number of related structures are reported [21, 24]. Presumably, complex V adopts a similar structure to III. In the solid state, Zn$(tmc)_2Cl_2$ (VI) adopts a six-coordinate structure [15, 52, 53] but, in solution, this complex dissociates into V and free tmc.

Experimental

Reagent grade chemicals were used in the preparation of tetramethylcarbohydrazide (tmc) and its complexes. Solvents were dried by standard methods and distilled under nitrogen before use. N,N-dimethylhydrazine was distilled from barium oxide. Triethylamine was distilled from calcium hydride. Phosgene was purified by trap-to-trap condensation on a vacuum line. Zinc chloride and cobalt chloride were dried in refluxing thionyl chloride. The latter salt was also dried by refluxing in acetone/2,2-dimethoxypropane.

Analyses were performed by the University Analyst, Simon Fraser University. The following instrumentation was employed: Gallenkamp and Fisher-Johns melting point apparatus; Radiometer (Copenhagen) conductivity meter, Type CDM2d and cell fitted with platinised platinum electrodes; Hitachi-Perkin Elmer Model 115 Molecular Weight Osmometer; Faraday Cahn electrobalance; Perkin Elmer 457 infrared spectrophotometer; Cary Model 17 and Cary Model 210 ultraviolet/visible spectrophotometers; Varian XL-100 and Bruker WM-400 NMR spectrometers.

Preparation of 1,1,5,5-Tetramethylcarbohydrazide

(a) The compound $Me_2NNHC(O)OSiMe_3$ (0.2 mol), synthesized according to the literature method [27], was sealed under vacuum in a two-liter flask. The flask was heated at 180 °C for three days and volatile products were separated by vacuum line fractionation into CO_2 (0.1 mol) and $(Me_3Si)_2O$ (0.095 mol), identified by IR and molecular weight measurements. The involatile residue remaining in the reaction vessel was purified by sublimation under vacuum and was identified as 1,1,5,5-tetramethylcarbohydrazide by analysis, IR (Tables I and II), ^1H NMR (τ(CH_3) at 7.47, τ(NH) at 4.01 ppm; in $CDCl_3$; relative intensity, 6:1); and ^{13}C NMR (δ(CO) at 157.6 ppm, δ(CH_3) at 47.6 ppm, in THF/acetone).

(b) The procedure of Wadsworth and Emmons [27] was modified as follows. A mixture of Me_2-

NNH_2 (4.1 mmol) and Et_3N (3.8 mmol) in THF (150 ml) was frozen in liquid nitrogen and the flask was pumped out on the vacuum line. Phosgene (1.7 mmol) was transferred to the flask, which was allowed to warm slowly to room temperature. Magnetic stirring was employed. After 24 hours, the solid $Et_3N{\cdot}HCl$ was filtered off. The filtrate was evaporated to dryness under vacuum and the tetramethylcarbohydrazide product was purified by sublimation under vacuum (oil bath temperature, 75 °C). Yield, 72%.

Preparation of Complexes

Co(tmc)Cl₂

The hydrated salt $CoCl_2{\cdot}6H_2O$ (1.47 mmol) was dried by refluxing in acetone/dimethoxypropane for 15 minutes. The solution was cooled and a deficient amount of tmc (1.02 mmol), in acetone, was added. Diethyl ether was added to effect precipitation, the blue solid $Co(tmc)Cl_2$ was filtered off, washed with acetone and dried. Yield, 62%. Molecular weight, M_{obs} = 272 (in acetone), M_{calc} = 276. Conductivity, Λ_M = 25.7 (in acetone), 19.9 Ω^{-1} cm^2 M^{-1} (in nitromethane). Electronic absorption spectrum (in acetone): 14,837 cm^{-1} (ϵ = 198 l M^{-1}, cm, 15.578(139), 16.863(107), 19.305(28). A similar spectrum was obtained using nujol mull. Magnetic moment, μ_{eff} = 4.9 B.M.

Co(tmc)₂Cl₂

The hydrated salt $CoCl_2{\cdot}6H_2O$ (1.43 mmol) was dried in refluxing acetone/2,2-dimethoxypropane (50 ml:10 ml). The solution was cooled and added dropwise to a stirred solution of tmc (2.88 mmol) in 50 ml of acetone. After 24 hours, the volume of solution was reduced to effect precipitation. The purple product $Co(tmc)_2Cl_2$ was filtered off, washed with acetone, and dried under vacuum. A second batch of $Co(tmc)_2Cl_2$ was obtained upon reducing the volume of the filtrate. Yield, 57%. Molecular weight in acetone, M_{obs} = 396, M_{calcd} = 422. Conductivity, Λ_M = 13.1 (in acetone) 27.7 Ω^{-1} cm^2 M^{-1} (in nitromethane). Electronic absorption spectrum (in acetone) 14.925 cm^{-1} (ϵ = 102 l M^{-1} cm), 15.480(93), 16.920(77), 18.215(53), 19.268(47), 20.243(32). The nujol mull spectrum showed an extremely weak band in the 15–20,000 cm^{-1} region. Magnetic moment, μ_{eff} = 5.1 B.M.

Zn(tmc)Cl₂

A solution of tmc (2 mmol) in acetone was added to a solution of $ZnCl_2$ (2 mmol) in 40 ml of acetone. The mixture was stirred for 24 hours, the volume was reduced under vacuum and hexane was added to induce precipitation. The white precipitate of $Zn(tmc)Cl_2$ was collected and dried under vacuum. Yield, 85%. Molecular weight (in acetone), M_{obs} = 305, M_{calcd} = 282.5. Conductivity, Λ_M = 6.8 (in acetone), 7.5 (in nitromethane). ^1H NMR spectrum (in acetone-d_6), $\tau(NH_a)$, 0.67, $\tau(NH_b)$, 1.93 ppm; $\tau(NMe_2)_a$, 7.06, $\tau(NMe_2)_b$, 7.42 ppm. ^{13}C NMR spectrum (in acetone), δ (CO), 160.6 ppm; and methyl ^{13}C resonances at 50.52, 50.43, 47.47 and 47.52 ppm.

Zn(tmc)₂Cl₂

A solution of $ZnCl_2$ (1.4 mmol) in acetone was added to an acetone solution of tmc (2.9 mmol). Upon adding hexane, the complex $Zn(tmc)_2Cl_2$ was precipitated immediately. Yield, 84%. Molecular weight (in acetone, M_{obs} = 273, M_{calcd} = 428.8. Conductivity, Λ_M = 7.5 (in acetone), 21.5 Ω^{-1} cm^2 M^{-1} (in nitromethane). ^1H NMR spectrum (in acetone-d_6), $\tau(NH)$, 2.09, $\tau(CH_3)$, 7.34 ppm. The NH resonance split into two peaks at 0 °C and the methyl resonance became a doublet at −15 °C. ^{13}C NMR spectrum (in acetone δ (CO), 159.0 ppm; δ (CH_3), 48.20 ppm.

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