

difficult to interpret. Phenanthroline itself shows weak to medium absorption at 240 and 257  $\text{cm}^{-1}$ . Two distinct patterns of spectra are observed in this region (Figure 2). The lighter members of the series from La to Sm show a spectra with several strong to medium bands located from 175 to 220  $\text{cm}^{-1}$ , with the strongest band at about 200  $\text{cm}^{-1}$ . From Eu to Lu several strong bands are observed in the 235- $\text{cm}^{-1}$  region. The shoulder at 242-248  $\text{cm}^{-1}$  might be associated with the ligand, rather than a metal-ligand vibration. These bands are tentatively assigned to  $\nu_{\text{M-N}}$  stretching vibrations, for the same reasons enumerated in the 2,2'-bipyridyl discussion. The most intense band for Sc is at 283  $\text{cm}^{-1}$ ; for Y it is at 263  $\text{cm}^{-1}$ . As in the bipyridyl complexes, a general trend toward higher frequency is noted with increasing atomic number. It is felt that this is related to the formation of stronger complexes. A typical spectrum, from 70 to 330  $\text{cm}^{-1}$ , of the heavier members of the series is illustrated in Figure 3. In Table IV are tabulated the tentative assignments of the metal-nitrogen stretching vibrations in this region.

Figure 4 shows a plot of the polarizing power *vs.* the position of this most intense band in the 200-300- $\text{cm}^{-1}$  region. A break at europium is observed. The curve is similar to the bipyridyl plot, but the rise starts at Sm rather than Eu. From Eu to Lu a rather flat line is obtained. Scandium and yttrium show absorption at higher frequency.

From Figure 4 it can be observed that the  $\nu_{\text{M-N}}$  vibration in the 2,2'-bipyridyl complexes for the lower members of the rare earth series is higher than

in the 1,10-phenanthroline complexes. In the higher members this is reversed. Based on published data with transition elements the 1,10-phenanthroline complexes would have been expected to form stronger complexes and to be found at higher frequencies than the bipyridyl compounds.<sup>13,14</sup>

In the region of 70-170  $\text{cm}^{-1}$  several medium to weak bands are found. 1,10-Phenanthroline shows absorption in this region, and assignments are more difficult to make. New absorptions occur at about 170 and 140  $\text{cm}^{-1}$ . With Sc and Y, bands are observed at about 170-212  $\text{cm}^{-1}$ , and no absorption occurs at 140  $\text{cm}^{-1}$ . As in the bipyridyl complexes some of the absorption in this region might be due to lattice vibrations. However, the bending NMN vibrations would also be expected in this region.

On the basis of the expected coordination number of 6 for the rare earths, it would be presumed that some of the water molecules and/or the chlorides are covalently coordinated. Some weak, broad absorptions are observed in the 300-600- $\text{cm}^{-1}$  region and could be due to coordinated water modes.<sup>15</sup> However, in view of the fact that no evidence for a metal chloride vibration is found from the infrared data, the metal-chloride link can be inferred to be ionic. Conductivity studies in most nonaqueous solvents are impossible because of the limited solubility of the complexes. The complexes are soluble in dimethylformamide and dimethyl sulfoxide but undergo decomposition.

(13) S. Cabani, G. Moretti, and E. Scrocco, *J. Chem. Soc.*, 88 (1962).

(14) B. R. James and R. J. P. Williams, *ibid.*, 2007 (1961).

(15) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 20, 429 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
WELLESLEY COLLEGE, WELLESLEY, MASSACHUSETTS 02181

## The Coordinate Bonding in Transition Metal Complexes of 2-Carbamoyldimedone

BY EMILY P. DUDEK AND MARY L. SNOW

Received September 13, 1965

A number of 2-carbamoyldimedone and N-phenyl-2-carbamoyldimedone complexes of the first transition metal series have been synthesized. The metal-ligand coordination has been investigated by spectral, magnetic, and proton and electron resonance measurements. The results indicate that the oxygen rather than the nitrogen of the carbamoyl group is coordinated to the metal ion. These findings are compared with the coordinate bonding reported for acetoacetamide and salicylamide complexes. Evidence of intermolecular bonding is presented, and a molecular structure is proposed.

### Introduction

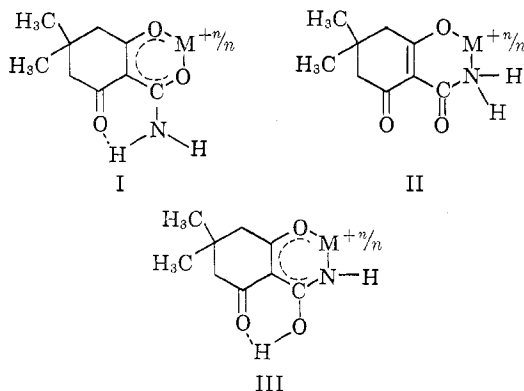
Since the metal-binding properties of tetracyclines, such as aureomycin and terramycin, may be related to the antibacterial action of the drugs, Albert and Rees determined the stability constants of several tetracycline-metal complexes.<sup>1</sup> The coordinating elements of the tetracyclines, however, have not been established.

(1) A. Albert, *Nature*, 172, 201 (1953); A. Albert and C. W. Rees, *ibid.*, 177, 433 (1956).

It is apparent that only one ring of a tetracycline is bonded to the metal, because the metal-ligand ratio is 1:2 for divalent metal ions and 1:3 for trivalent metal ions. The high acidity of the enolic proton of the diketoamide portion of a tetracycline ( $\text{p}K_a = 3.30$  for aureomycin<sup>2</sup>) as compared to that of the other acidic protons ( $\text{p}K_a = 7.44, 9.27$  for aureomycin<sup>2</sup>) suggests

(2) L. J. Leeson, J. E. Krueger, and R. A. Nash, *Tetrahedron Letters*, 1155 (1963).

that it is the diketoamide group which participates in the coordinate bonding. To investigate the bonding between transition metal ions and the diketoamide grouping, we have studied the coordinate bonding in complexes of the simpler model system, 2-carbamoyldimedone (2-carbamoyl-5,5-dimethylcyclohexane-1,3-dione). The model embodies the diketoamide moiety but contains no other interfering functional groups which could complicate chemical studies. Nevertheless, even this simpler system offers more than one possibility of metal-ligand linkage as indicated by the three structures



We wish to present here evidence in support of I.

2-Carbamoyldimedone (0.01 mole), sodium acetate (0.01 mole), and the divalent metal acetate hydrate (0.005 mole) were refluxed in about 200 ml of 95% ethanol for 12 hr. The ethanol was then evaporated to yield the product in a powdered form. The material was washed with water and with benzene. It was then recrystallized from the appropriate solvent, except in the case of bis(2-carbamoyldimedonato)copper(II), which we found to be insoluble.

The complexes of N-phenyl-2-carbamoyldimedone were prepared by dissolving N-phenyl-2-carbamoyldimedone (0.02 mole) in chloroform and combining the chloroform solution with a saturated aqueous solution of the metal acetate (0.01 mole). The crude product was precipitated out, filtered, and recrystallized from the appropriate solvent.

**Infrared Spectra.**—Spectra were obtained on Perkin-Elmer Model 237 and 337 grating spectrometers. The instruments were calibrated with the aid of polystyrene film, and the wavelengths are accurate to  $\pm 2$   $\text{cm}^{-1}$ . Spectra of the 4000–1250- $\text{cm}^{-1}$  region were recorded for Flucrolube mulls using sodium chloride plates, and spectra of the 1250–400- $\text{cm}^{-1}$  region were recorded for Nujol mulls using potassium bromide plates. The complexes were not soluble enough for solution studies.

**Proton Resonance Spectra.**—Spectra were taken on a Varian A-60 spectrometer operating at 60.00 Mc (sample temperature 31°). The reference was internal tetramethylsilane, and the chemical shifts were given in ppm downfield from this point ( $\delta$  scale). The spectra were calibrated by extrapolation from an adjacent side band of TMS generated by an audio oscillator. The stability of the spectrometer rendered the usual procedure of interpolating between the two side bands unnecessary (the accuracy of the sweep circuit was also checked). The oscillator was continuously monitored by a frequency counter. The data

TABLE I  
CHARACTERIZATION OF N-SUBSTITUTED 2-CARBAMOYLDIMEDONE COMPLEXES OF SOME TRANSITION METALS<sup>a</sup>

Compd	Dec pt, °C <sup>b</sup>	Yield, %	% C		% H		% N		Purification
			Calcd	Found	Calcd	Found	Calcd	Found	
Bis(2-carbamoyldimedonato)copper(II) <sup>c</sup>	325–326	87	...	...	...	...	...	...	Washed with methanol and hot water
Bis(2-carbamoyldimedonato)nickel(II)	338	77	51.10	50.75	5.72	5.62	6.62	6.70	Recrystallized from ethanol-water as hydrate, dried <i>in vacuo</i>
Bis(2-carbamoyldimedonato)cobalt(II)	304–305	70	51.07	50.94	5.71	5.83	6.62	6.75	Same as analogous nickel complex
Bis(2-carbamoyldimedonato)zinc(II)	283–285	77	50.30	49.89	5.63	4.84	6.52	6.45	Recrystallized from ethanol
Tris(2-carbamoyldimedonato)iron(III)	260–270 (mp) <sup>d</sup>	...	...	...	...	...	...	...	Recrystallized from chloroform- <i>n</i> -heptane
Bis(N-phenyl-2-carbamoyldimedonato)copper(II) <sup>e</sup>	309–310	68	...	...	...	...	...	...	Recrystallized from chloroform
Bis(N-phenyl-2-carbamoyldimedonato)nickel(II)	>360	75	62.63	61.77	5.61	5.54	4.87	4.83	Recrystallized from ethanol
Bis(N-phenyl-2-carbamoyldimedonato)cobalt(II)	355	66	62.63	62.88	5.61	5.79	4.87	4.75	Recrystallized from ethanol
Bis(N-phenyl-2-carbamoyldimedonato)zinc(II)	305–309	82	61.91	61.52	5.61	5.13	4.87	4.79	Recrystallized from ethanol

<sup>a</sup> Mass spectra of all of the compounds have been recorded, and the observed parent peaks correspond to the anticipated molecular weights: E. P. Dudek and M. Barber, *Inorg. Chem.*, **5**, 375 (1966). <sup>b</sup> All compounds decomposed before melting. <sup>c</sup> Previously prepared by Scarborough and Gould, ref 3. <sup>d</sup> Prepared from iron(III) chloride. The compound could not be obtained in a crystalline form owing perhaps to the presence of a racemic mixture. Its infrared and ultraviolet spectra were similar to those of analogous compounds, and its mass spectrum indicated that the compound had the correct molecular weight. <sup>e</sup> Previously prepared by Shemyakin, *et al.*, ref 4.

### Experimental Section

**Chemicals.**—Chloroform-*d* and dimethyl sulfoxide-*d*<sub>6</sub> were supplied by Merck Sharpe and Dohme of Canada. The calibrant for magnetic susceptibility measurements, mercury tetrathiocyanatocobalt(II), HgCo(SCN)<sub>4</sub>, was obtained from Eastman Organic Chemicals.

**Synthesis of Compounds. Ligands.**—2-Carbamoyldimedone (2-carbamoyl-5,5-dimethylcyclohexane-1,3-dione) was synthesized by the procedure of Scarborough and Gould.<sup>3</sup>

N-Phenyl-2-carbamoyldimedone was prepared according to the method of Shemyakin, *et al.*<sup>4</sup>

**Complexes.**—The metal complexes of 2-carbamoyldimedone listed in Table I were prepared by the following general method.

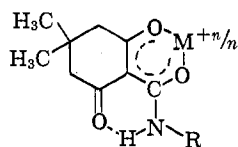
(3) H. C. Scarborough and W. A. Gould, *J. Org. Chem.*, **26**, 3720 (1961).

(4) M. M. Shemyakin, Yu. A. Arbutov, M. N. Koloxov, G. A. Shatenstein, V. V. Onoprienko, and Yu. V. Konnova, *Zh. Obshch. Khim.*, **30**, 542 (1960).

are good to 0.6 cps or 0.01 ppm except where band width precluded such accuracy. All solutions were 10% w/v in dimethyl sulfoxide-*d*<sub>6</sub>. The low solubility of the complexes limited the choice of solvent to dimethyl sulfoxide.

**Electron Paramagnetic Resonance Spectra.**—Spectra were obtained with a Varian V-4502 epr spectrometer system employing 100-kc/sec modulation and detection and operating at about 9.5 Gc. The Klystron frequency was measured with a transfer oscillator and frequency counter. The magnetic field was measured by means of a proton gauss meter monitored by the same frequency counter. The samples were diluted chloroform-*d* solutions (not degassed). All spectra were recorded at room temperature.

**Ultraviolet-Visible Spectra.**—Spectra were taken on a Cary Model 14 recording spectrometer. Methanol was the solvent used for solution measurements. The solid samples were Kaydol mulls. All data were obtained at room temperature.

TABLE II  
 INFRARED (CM<sup>-1</sup>)<sup>a</sup> AND ULTRAVIOLET-VISIBLE DATA FOR COMPOUNDS OF THE GENERAL FORMULA


R	M	n	Free N—H stretch	Bonded N—H stretch	Uncoordinated C=O stretch	Coordinated C=O stretch	$\lambda_{\max}$ , m $\mu$ <sup>b</sup>	$10^4 \epsilon_{\max}$ <sup>b</sup>	$\lambda_{\max}$ , m $\mu$ <sup>c</sup>	$\bar{\nu}$ , cm <sup>-1</sup>	Relative intensity <sup>c</sup>
H	H	1	3340 (m)	3210 (vw, b)	1640 (s)	1575 (s)	259	1.84			
H	Cu	2	3330 (m)	3160 (vw)	1600 (sh)	1575 (s)	290 (sh) <sup>e</sup>				
							262				
H	Ni	2	3370 (m)	3275 (m)	1610 (sh)	1580 (s)	267	3.47	410 (sh)	24,400	1.00
							246 (sh)	2.94	630	15,900	0.50
									750 (sh)	13,300	0.40
									1230 (b)	8,150	0.40
H	Co	2	3335 (m)	3210 (vw)	1615 (m)	1580 (s)	261	3.30	410 (sh)	24,400	1.00
									530	18,900	0.71
									1170	8,550	0.06
H	Zn	2	3340 (m)	3160 (vw)	1610 (sh)	1580 (s, b)	263	3.32			
							248 (sh)	2.54			
H	Fe	3	3340 (m)	3150 (vw, b)	1600 (m)	1565 (s)	258 <sup>d</sup>	5.60			
							235 (sh)	4.06			
C <sub>6</sub> H <sub>5</sub>	H	1	...	3055 (w, b)	1640 (m)	1580 (s)	273	2.46			
C <sub>6</sub> H <sub>5</sub>	Cu	2	...	3010 (w, b)	1610 (m)	1575 (s)	277 <sup>e</sup>	5.97			
C <sub>6</sub> H <sub>5</sub>	Ni	2	...	3015 (w, b)	1610 (m)	1580 (s)	276	5.96	400	25,000	1.00
									622	16,100	0.50
									730 (sh)	13,700	0.39
									1180 (b)	8,500	0.38
C <sub>6</sub> H <sub>5</sub>	Co	2	...	3025 (w, b)	1620 (m)	1590 (s)	273	5.81	430	23,300	1.00
									495	20,200	0.66
									520	19,200	0.74
									555	18,000	0.58
									1150	8,700	0.16
C <sub>6</sub> H <sub>5</sub>	Zn	2	...	3010 (w, b)	1620 (m)	1590 (s)	274	6.08			

<sup>a</sup> s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad; d, doublet. <sup>b</sup> Methanol solution unless otherwise stated. <sup>c</sup> Kaydol mull. <sup>d</sup> Also,  $\lambda_{\max}$  390 m $\mu$ ,  $\epsilon_{\max}$   $4.15 \times 10^3$ ;  $\lambda_{\max}$  305 m $\mu$ ,  $\epsilon_{\max}$   $1.30 \times 10^4$ . <sup>e</sup> In Kaydol mull  $\lambda_{\max}$  272 m $\mu$ .

**Magnetic Measurements.**—Determinations of magnetic susceptibilities were made at various field strengths and at room temperature (about 24°) using the Gouy method. The calibrant was mercury tetrathiocyanatocobalt(II).<sup>5</sup> The magnetic moments reported in Table VI are corrected for diamagnetic contributions.<sup>6</sup> Because of the low solubility of the complexes, magnetic measurements of solutions could not be made.

## Results

**Infrared Spectra.**—The 2-carbamoyldimedone complexes exhibit the two N—H stretching absorptions (Table II) of the uncoordinated ligand with only a little variation in frequency. This suggests that in the complexes the amine group is present as opposed to an imine form and that the amine group is not bonded to the metal. The absorption in the region 1700 to 1600 cm<sup>-1</sup> is designated the uncoordinated carbonyl stretch and attributed to the carbonyl group of position 3 since 2-acetyldimedone displays an absorption in this region whereas 2-acetylcyclohexanone does not. There are two small shifts in stretching frequencies upon coordination of N-phenyl- or unsubstituted 2-carbamoyldimedone to a metal ion. They are a decrease in the uncoordinated C=O stretching frequency and a de-

crease in the bonded N—H stretching frequency. Apparently, the coordination of the metal ion to the amide oxygen enhances the hydrogen bonding between an amide hydrogen and the carbonyl group in position 3 of the dimedone ring (structure I). When the amide oxygen is not coordinated to the metal ion as in the sodium and barium salts of 2-carbamoyldimedone, the change in the uncoordinated carbonyl stretching frequency is much less, being at 1633 cm<sup>-1</sup> for the sodium and 1635 cm<sup>-1</sup> for the barium derivative. On the other hand, if structure II were correct, the carbonyl frequency would presumably increase upon coordination to the metal ion since the intramolecular hydrogen bonding would not be possible.

In comparing the N—H stretching frequencies of the 2-carbamoyldimedone metal complexes, it is noted that the absorptions of the nickel compound are at significantly higher frequencies, and both bands are intermediary in intensity. This peculiar feature of the nickel complex may be due to intermolecular bonding, in which the amide nitrogen is bonded to nickel since the N—H stretches are similar to those reported for nickel-amino acid complexes.<sup>7</sup>

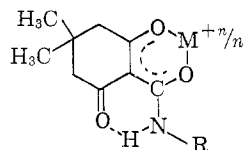
**Proton Magnetic Resonance Spectra.**—The nmr

(5) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).  
 (6) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 403.

(7) I. Nakagawa, R. J. Hopper, J. L. Walter, and T. J. Lane, *Spectrochim. Acta*, **21**, 1 (1965).

spectra (see Table III) of 2-carbamoyldimedone and N-phenyl-2-carbamoyldimedone and their zinc complexes indicate that the coordination of the dimedone derivatives to a metal ion produces the following changes: (1) disappearance of the resonance of the enolic hydrogen, (2) a greater differentiation between the chemical shifts of the two methylene groups, and (3) maintenance of the resonances of the amine group.

TABLE III  
PROTON MAGNETIC RESONANCE DATA FOR COMPOUNDS  
OF THE TYPE<sup>a</sup>



R	M	Di-methyl	Methylene	R	N-H	O-H
H	H	1.01	2.40 (b)	8.50	9.15	18.38
H	Zn	0.98	2.30, 2.50	7.50	9.63	...
C <sub>6</sub> H <sub>5</sub>	H	1.00	2.40 (b)	7.40 <sup>b</sup>	11.8	17.65
C <sub>6</sub> H <sub>5</sub>	Zn	0.98	2.30, 2.50	7.50 <sup>b</sup>	12.9	...

<sup>a</sup> Dimethyl sulfoxide-*d*<sub>6</sub> solvent in ppm downfield from tetramethylsilane at 60.00 Mc. <sup>b</sup> Multiplet.

The two N-H absorptions rule out the imine form. The small downfield shift of the hydrogen-bonded amine proton indicates that the hydrogen bonding of the amine proton is increased (form I) on coordination of the amide oxygen to the metal ion. If the nitrogen of the ligand were bonded to the metal ion as in form II, neither amine proton would exhibit the low-field chemical shift characteristic of hydrogen-bonded protons.

The most direct way of distinguishing between structures I, II, and III might well have been an nmr study of the contact and pseudo-contact shifts of the Ni(II) and Co(II) compounds. The limited solubilities of the complexes, however, prevented such investigations. Even at 100°, a saturated dimethyl sulfoxide-*d*<sub>6</sub> solution of bis(N-phenyl-2-carbamoyldimedonato)nickel(II) showed no proton resonance.

**Electron Paramagnetic Spectra.**—The epr data are given in Table IV. The spectrum of bis(N-phenyl-2-carbamoyldimedonato)copper(II) is a quartet due to the coupling of the electron spin with the copper nucleus of  $I = 3/2$ . There is no observable hyperfine splitting due to nitrogen. The line width at half-peak height is 10 gauss whereas the nitrogen hyperfine splitting is 12.0 gauss for bis(2-acetiminodimedonato)copper(II)<sup>8</sup> and 10.8 gauss for bis(salicylamidato)copper(II).<sup>9</sup> Furthermore, at liquid nitrogen temperature where ligand exchange has been quenched, still no coupling with the nitrogen nuclei is evident, the line width at half-peak height being 6 gauss. Hence, the epr results indicate that the copper is not bonded to nitrogen but instead the all-oxygen-coordinated structure, I, is correct.

(8) E. P. Dudek, to be published.

(9) A. K. Wiersema and J. J. Windle, *J. Phys. Chem.*, **68**, 2316 (1964).

TABLE IV  
ELECTRON PARAMAGNETIC RESONANCE DATA

	<i>g</i> <sub>0</sub>	Cu hyperfine splitting, gauss	N hyperfine splitting, gauss
Bis(N-phenyl-2-carbamoyldimedonato)copper(II) <sup>a</sup>	2.126	78.7	...
Bis(acetoacetanilidato)copper(II)	2.128	79.0	...
Bis(salicylamidato)copper(II) <sup>b</sup>	2.12	~80.0	~15.0
Bis(2-acetiminodimedonato)copper(II)	2.101	64.8	12.0

<sup>a</sup> Bis(2-carbamoyldimedonato)copper(II) was not sufficiently soluble in CDCl<sub>3</sub> to yield a detectable epr signal. <sup>b</sup> See ref 9.

The *g* values and hyperfine splitting measurements are given in Table IV. The data for the copper complexes of N-phenyl-2-carbamoyldimedone and acetoacetanilide are nearly equal, suggesting that the coordinate bonding in the two complexes is the same. The relatively low *g* value for bis(2-acetiminodimedonato)copper(II) is indicative of a larger crystal field splitting,<sup>10</sup> and the smaller hyperfine splitting produced by the copper nucleus depicts a greater delocalization of the unpaired electron of the copper in the imino compound.

**Ultraviolet Spectra.**—There is only a slight increase in the wavelength of the absorption of 2-carbamoyldimedone or N-phenyl-2-carbamoyldimedone upon coordination of either compound to a metal ion. Complexation increases the intensity of the absorption. The molar extinction coefficients (given in  $M^{-1} \text{ cm}^{-1}$ , Table II), for the bivalent metal complexes of N-phenyl-2-carbamoyldimedone are more than twice that of the uncoordinated ligand, and, although the coefficients of the corresponding 2-carbamoyldimedone complexes are not twice as large as  $\epsilon_{\text{max}}$  of the ligand, the absorption bands are broader and for all but the cobalt(II) complex two absorptions are observed, one appearing as a shoulder to the principal band.

The spectra of bis(2-carbamoyldimedonato)nickel(II) and (N-phenyl-2-carbamoyldimedonato)nickel(II) indicate that in the solid state the nickel ions are in a weak, quasi-octahedral ligand field with  $Dq = 815$  and  $850$ , respectively. The near-infrared absorption at  $\sim 8300 \text{ cm}^{-1}$  supports an octahedral configuration as opposed to a square-planar form. The six-coordinate complexes must result from intermolecular bonding. This bonding does not produce a symmetric octahedral structure since the low intensity of the  $8300\text{-cm}^{-1}$  band and the high-energy value of the absorption near  $16,000 \text{ cm}^{-1}$  are not expected for a field of  $O_h$  symmetry.<sup>11</sup> (For example, bis(N-phenyl-2-carbamoyldimedonato)nickel(II) with ligand field of  $Dq = 850$  and  $O_h$  symmetry: calcd  $13,500$ , obsd  $13,700 \text{ cm}^{-1}$ ; calcd  $15,400$ , obsd  $16,100 \text{ cm}^{-1}$ ; calcd  $25,300$ , obsd  $25,000 \text{ cm}^{-1}$ .) The low intensity of the  $8300\text{-cm}^{-1}$  band suggests that the ligand field is tetragonal<sup>12</sup>

(10) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)*, **A205**, 135 (1951).

(11) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6**, 134 (1959).

(12) L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, **4**, 818 (1965).

with the longer intermolecular bonds oriented along the fourfold-symmetry axis.

The solid-state spectra of the two cobalt complexes also support a tetragonal structure. The absorptions at  $\sim 8500$  and  $\sim 19,500$   $\text{cm}^{-1}$  are characteristic of octahedral cobalt(II) complexes, and the splitting of the latter band in the bis(N-phenyl-2-carbamoyldimedonato)cobalt(II) spectrum is indicative of tetragonal distortion.<sup>13</sup> The absorptions at  $\sim 24,000$   $\text{cm}^{-1}$  are at too high a frequency for ligand-field transitions but are not observed in the solid-state spectra of the uncoordinated ligands. Possibly they are charge-transfer bands.

**Magnetic Moments.**—The magnetic moments listed in Table V for solid samples of 2-carbamoyldimedone- and N-phenyl-2-carbamoyldimedone-metal complexes denote an octahedral ligand field about each metal ion. The 3.22 and 3.24 BM values for the nickel complexes negate a diamagnetic, square-planar structure, and yet the moments are not as high as values reported for most tetrahedral nickel complexes.<sup>14</sup>

TABLE V  
MAGNETIC MOMENTS OF SOLID SAMPLES<sup>a</sup>

	$\mu_{\text{eff}}$ , BM
Bis(2-carbamoyldimedonato)copper(II)	1.96
Bis(2-carbamoyldimedonato)nickel(II)	3.22
Bis(2-carbamoyldimedonato)cobalt(II)	5.18
Bis(N-phenyl-2-carbamoyldimedonato)copper(II)	1.97
Bis(N-phenyl-2-carbamoyldimedonato)nickel(II)	3.24
Bis(N-phenyl-2-carbamoyldimedonato)cobalt(II)	5.09

<sup>a</sup> All values obtained at ambient room temperature,  $24 \pm 2^\circ$ . Estimated error  $\pm 2\%$ .

### Conclusion

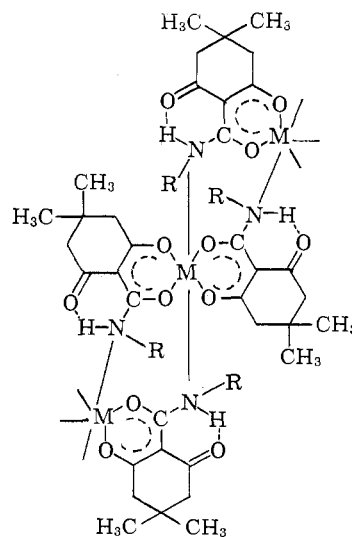
The spectroscopic data indicate that in metal complexes of N-substituted 2-carbamoyldimedone the metal is coordinated to two oxygen atoms of each ligand as presented in form I. The imine structure, III, is ruled out since the two N-H absorptions in the infrared and nmr spectra of 2-carbamoyldimedone are still observed in the spectra of the complexes. The decrease in the carbonyl stretching frequencies and the increase in the hydrogen bonding of one amine proton refute the nitrogen-coordinated structure of II. Furthermore, the absence of nitrogen hyperfine splitting in the epr spectrum of bis(N-phenyl-2-carbamoyldimedonato)copper(II) supports the all-oxygen-coordinated structure, I. It is suggested that the all-oxygen-coordinated form is the preferred structure owing to conjugation in the chelate ring, a resonance which is not possible in the nitrogen-bonded amine form, II. According to Wiersema and Windle,<sup>9</sup> salicylamide is joined to copper by the amine nitrogen; however, in the salicylamide complex, conjugation in the all-oxygen-coordinated chelate ring would compete with the resonance in the aromatic system.

The structure proposed for the N-substituted 2-carbamoyldimedone complexes is similar to that pre-

sented by Wolf and Wetzel<sup>15</sup> for acetoacetamide-metal compounds and that given by Belford, *et al.*,<sup>16</sup> for bis-(N,N-diethylacetoacetamidato)copper(II). The former authors based their argument on the linear relationship found between the acid dissociation constants of the enol form of the acetoacetamide derivatives and the first dissociation constant of the corresponding copper complexes, and they ruled out the imine structure by preparing N,N-disubstituted acetoacetamide complexes. The latter authors favored the all-oxygen-coordinated form since the ultraviolet curves of the copper complexes of ethyl acetoacetate and N,N-diethylacetoacetamide were superimposable. Thus, it appears that oxygen is the only coordinating element in complexes of acetoacetamide derivatives, N-substituted 2-carbamoyldimedone being included in this category, but in salicylamide-copper complexes where the aromatic resonance competes with conjugation in the metal chelate ring, the nitrogen is bonded to copper.

The solid-state magnetic moments and ultraviolet-visible spectra of the N-substituted 2-carbamoyldimedone complexes reveal extensive intermolecular bonding giving rise to a quasi-octahedral ligand field. The low solubility and high decomposition points are also indicative of such intermolecular association. In the case of tris(2-carbamoyldimedonato)iron(III) where the metal is in an octahedral environment and intermolecular bonding is sterically hindered, the solubility of the compound is significantly greater, and its melting point is about  $270^\circ$ . Since bis(2-acetyldimedonato)copper(II)<sup>17</sup> is much more soluble and melts  $60^\circ$  lower than bis(2-carbamoyldimedonato)copper(II), the intermolecular association in the latter complex is presumably *via* the nitrogen of the carbamoyl moiety. Such association may be responsible for the high N-H stretching frequencies of bis(2-carbamoyldimedonato)nickel(II). Unfortunately, the low solubility of the compound prevented solution studies of the bonding.

On the basis of all of the spectroscopic and magnetic



(15) L. Wolf and K. Wetzel, *Chem. Ber.*, **90**, 1007 (1957).

(13) C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955).

(14) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

(16) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1958).

(17) H. Smith, *J. Chem. Soc.*, 803 (1953).

measurements, the following structure is proposed for an N-substituted 2-carbamoyldimedone-metal complex with a metal-ligand ratio of 1:2.

**Acknowledgment.**—We thank Dr. Gerald O. Dudek

for helpful suggestions. We are indebted to Harvard University for the use of various instruments. This work was supported in part by the National Science Foundation Undergraduate Research Program (Grant No. GE-2753).

CONTRIBUTION FROM THE INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY,  
UNIVERSITY OF FLORENCE, FLORENCE, ITALY

## Five-Coordinated Structure of Bis(N-methylsalicylaldiminato)zinc(II); Isomorphism with the Cobalt(II) and Manganese(II) Analogs

BY P. L. ORIOLI, M. DI VAIRA, AND L. SACCONI

Received August 3, 1965

The crystal structure of bis(N-methylsalicylaldiminato)zinc(II) has been determined by three-dimensional X-ray analysis. The structure consists of dimers with symmetry  $C_i$ , in which the metal atom shows the coordination number of five. The configuration around the metal atom can be described as a distorted trigonal bipyramid. The Mn(II) and Co(II) derivatives are isomorphous with the Zn(II) complex.

### Introduction

The ligand N-methylsalicylaldimine forms complexes with many bivalent 3d metals, having the general formula bis(N-methylsalicylaldiminato)metal(II):  $(C_6H_4OCHNHCH_3)_2M^{II}$ . So far only the structure of the  $\beta$  form of the nickel(II) complex<sup>1</sup> and of the  $\alpha$  form of the copper(II) complex<sup>2</sup> have been determined by X-ray analysis. Both complexes have a square-planar configuration.

For the Co(II) and Zn(II) complexes a tetrahedral structure would be expected, on the basis of previous knowledge of the stereochemistry of four-coordinated complexes of these two metals with salicylaldimines.<sup>3</sup> Nevertheless, the reflectance spectrum of bis(N-methylsalicylaldiminato)cobalt(II) could not be interpreted on the basis of a tetrahedral structure.<sup>4</sup> For this reason we have undertaken an X-ray investigation of these complexes, in order to establish their molecular stereochemistry.

In a previous communication<sup>5</sup> we have reported preliminary results on the structure of bis(N-methylsalicylaldiminato)zinc(II) and we have shown the cobalt(II) and manganese(II) analogs to be isomorphous with the zinc complex. We wish now to report the final results of the three-dimensional X-ray analysis of the zinc(II) complex.

This compound has been chosen in preference to the others because it is insensitive to air exposure, while the others tend to decompose.

(1) E. Frasson, C. Panattoni, and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959).

(2) E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Scheringer, and C. Freiburg, *Acta Cryst.*, **14**, 1222 (1961).

(3) (a) L. Sacconi and P. L. Orioli, *Ric. Sci.*, **32 (II-A)**, 645 (1962); (b) E. Frasson and C. Panattoni, *Z. Krist.*, **116**, 154 (1961).

(4) L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, **87**, 3102 (1965).

(5) P. L. Orioli, M. Di Vaira, and L. Sacconi, *Chem. Commun. (London)*, **6**, 103 (1965).

### Experimental Section

The compounds were prepared by reaction between the metal salicylaldehydates and methylamine in methanol solution. Suitable crystals were obtained by slow evaporation from solutions in chloroform. The crystals of the three complexes are identical in shape, but different in color (Mn, orange; Co, emerald-green; Zn, straw yellow).

Cell dimensions were determined from rotation and Weissenberg photographs using Fe  $K\alpha$  radiation ( $\lambda$  1.9373 Å) for the Mn(II) and Co(II) complexes and Cu  $K\alpha$  radiation ( $\lambda$  1.5418 Å) for the Zn(II) complex. The NaCl rotation pattern ( $a = 5.6387$  Å) was superimposed on all the photographs for calibration. The results are shown in Table I. The space group was assumed to be  $P\bar{1}$  and confirmed by the structural analysis. Visual examination of the X-ray photographs of the three complexes revealed no detectable differences in intensities.

Three-dimensional X-ray analysis was undertaken on the zinc compound, using Cu  $K\alpha$  radiation. The crystal chosen had dimensions:  $0.20 \times 0.15 \times 0.40$  mm. Double integrated Weissenberg photographs  $h\bar{k}0$  through  $h\bar{k}6$  were taken on a Nonius integrating camera, using the multiple film equiinclination technique. The intensities of the reflections were measured on a Nonius microdensitometer, the density being assumed proportional to the intensity of the reflections; 2478 independent reflections were examined, about 75% of the total number in the Cu sphere of reflection.

Of these, 617 were found to be too weak to be measured and were assigned half of the minimum observable intensity. All intensities were corrected for Lorentz and polarization effects.

The three reflections  $2\bar{2}1$ ,  $\bar{1}21$ , and 101 were later considered affected by secondary extinction and not included in the least-squares refinement. No correction was made for absorption.

The atomic scattering factors were taken from Cromer.<sup>6</sup> The zinc scattering factor was corrected for the real part of the anomalous dispersion ( $\Delta f' = -1.7$  for Cu  $K\alpha$ ).

All calculations were performed on an IBM 1620 with a set of programs written by Albano, Bellon, Pompa, and Scatturin.<sup>7</sup>

(6) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(7) (a) V. Albano, P. L. Bellon, and F. Pompa, *Ric. Sci.*, **33**, 285 (1963); (b) V. Albano, P. L. Bellon, F. Pompa, and V. Scatturin, *ibid.*, **33**, 1067 (1963).