SYNTHESIS OF THE METAL COMPLEXES OF THE SCHIFF BASE DERIVED FROM 2,3-DIAMINO-*CIS*-2-BUTENEDINITRILE AND SALICYLALDEHYDE

MASASHI TAKAHASHI and TOSCHITAKE IWAMOTO*

Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

(Received 10 December 1979; received for publication 10 March 1980)

Abstract—A novel series of metal (Mn(II), Fe(III), Co(II). Ni(II), Cu(II). Zn(II) and Pd(II)) complexes of the Schiff base ligand derived from 2.3-diamino-*cis*-2-butenedinitrile (diaminomaleonitrile) and salicylaldehyde have been prepared by the template reaction in the solution containing the metal halide, the diamine, and the aldehyde in a 1:1:2 ratio. A characteristic feature has been observed in their Raman spectra.

INTRODUCTION

Diaminomaleonitrile (damn: 2,3-diamino-cis-2-butenedinitrile) has been known as an unsaturated electronrich ligand and as a tetramer of hydrogen cyanide, the tetramer which has been suggested one of the important prebiotic compounds. However, there have been only a few papers describing the metal complex chemistry related to damn[1-4]. Generally, damn behaves unsymmetrically in several organic and metal complex formation reactions in spite that its formula (H₂N)(NC) C=C(CN)(NH₂) appears to be rather symmetric. It reacts with aldehyde to give only a 1:1 Schiff base even in the presence of excessive amounts of the aldehyde [5]; it is unidentate in *trans* [PdCl₂ (damn)₂][1]. As has been reported in our previous communication[6], we have been undertaking the synthetic investigations of the metal complexes of Schiff base ligands derived from damn. The Cu(II) complex of bis (salicylideneamino) maleonitrile [H₂dss: (2,3-dinitrilo-cis-2-butene-2,3diiminomethyl) di-o-phenol] was prepared by the template reaction among a Cu(II) ion, a damn molecule, and two salicylaldehyde molecules[6]. The H₂dss itself has never been isolated by the reaction between damn and excessive amounts of salicylaldehyde; the product was always 1-amino-2-salicylideneaminomaleonitrile (Hds: 2amino-2,3-dinitrilo-cis-2-butene-3-iminomethyl-o-phenol). The template reaction was applied for other metals such as Mn(II), Fe(II), Co(II), Ni(II), Pd(II) and Zn(II) to prepare the metal complexes of the dss² ligand. This paper will describe the synthetic investigation of these metal complexes including that of Cu(II).

EXPERIMENTAL

The damn kindly supplied by Kyowa Gas Chemical Industry Co., Ltd., was recrystallized three times from hot water in the presence of active charcoal, and then recrystallized from hot pure water. The temperature of the solution should not be raised up higher than 70° C, because some portions of damn decompose in too hot solution.

A Hitachi EPS-ST spectrophotometer was used to record absorption spectra of solution samples in 200–800 nm region. IR spectra were recorded on a JASCO DS403G spectrophotometer for the Nujol and the hexachlorobutadiene mulls. Raman spectra were recorded on a JEOL JRS400D double-monochromated spectrophotometer for crystalline powder samples on rotating holder and for solution samples in glass capillaries using 488.0 and 514.5 nm lines from a JEOL argon ion laser as the exciting radiations. Magnetic susceptibilities of powder samples were measured by Gouy method at ambient temperature; the temperature dependency in the lower temperature region was measured by Faraday method[7]. The elemental analyses for C, H and N were done at the laboratory of elemental analysis. Department of Chemistry, Faculty of Science of this University. The metal contents were determined chelatometrically after decomposition of solid samples with nitric acid and hydrogen peroxide at elevated temperature.

Preparation of metal complexes. [Cu dss]: Although several reaction conditions were examined in the previous communication[6], the most recommendable procedure is as follows: A hot solution of damn (0.432 g, 4 mmol) in 95% ethanol (EtOH: 25 ml), and a hot solution of salicylaldehyde (Hsal: 0.976 g, 8 mmol) in 15 ml EtOH are successively added into a hot solution of CuCl₂ · 2H₂O (0.682 g, 4 mmol) in 50 ml of EtOH kept at 70°C on a steam bath. By heating the mixed solution for a few min, wine red needle-like crystals are formed. After heating for 10 more min, the crystals are filtered out from the hot solution, washed with hot EtOH, and dried in a silica gel desiccator (70% yield). Calc. For C₁₈H₈N₄O₂Cu: C 57.22; H, 2.67; N, 14.83; Cu, 16.8 Found: C, 57.25, H 2.59: N, 14.84: Cu 16.8%. ν_{max}/10 cm^{-1} (absorption maxima of EtOH solution in $kK = 10^3 cm^{-1}$), $(\log \varepsilon)$: 45.7, (4.7); 38.6, (4.5); 32.5, (4.4); 27.5, (4.5); 26.5, (4.3); 20.0, (4.2). μ_{eff}/B.M. 1.92.

[Ni dss]: By the procedure similar to that for [Cu dss] but using 4 mmol of NiCl₂ · 6H₂O, purple needles of [Ni dss] were obtained (70% yield). Calc. for C₁₈H₈N₄O₂Ni: C. 57.96; H. 2.70; N, 15.02; Ni, 15.7. Found: C. 57.91; H. 2.87; N, 14.98; Ni, 15.7%. $\nu_{\text{max}}^{\text{EroH}}$ (log ε): 43.7, (4.7); 39.2, (4.8); 33.2, (4.6); 26.6, (4.3); 23.1, (4.4); 19.0, (4.2); 16.7, (3.8). Diamagnetic.

[Pd dss]: A hot solution of damn (0.108 g, 1 mmol) in 25 ml of EtOH and a hot solution of Hsal ((0.244 g, 2 mmol) in 15 ml of EtOH were added successively to a hot solution of Na₂ [PdCl₄] (0.348 g, 1 mmol) in 75 ml of EtOH. The mixed solution was treated similarly to the way for the Cu(II) complex to give purple needles of [Pd dss] (85% yield). Calc. for $C_{18}H_8N_4O_2Pd$: C, 51.39; Pd, 25.1, Found: C, 50.82; H, 2.24; N, 12.93; Pd, 25.1, ν_{max}^{EOH} . (log ϵ): 44.6, (4.7); 39.8, (4.4); 35.2, (4.5); 30.8, (4.1); 26.4, (4.3); 24.9, (4.4); 18.7, (4.2). Diamagnetic.

[Co dss] \cdot C₂H₅OH and [Zn dss] \cdot C₂H₅OH: The mixture solution of damn (4 mmol). Hsal (8 mmol), and CoCl₂ \cdot 6H₂O (0.592 g, 4 mmol) in *ca.* 115 ml of EtOH was prepared with the way similar to the above-mentioned, and heated for 5 min on a steam bath. By adding a few ml of triethylamine to the solution, dark purple

^{*}Author to whom correspondence should be addressed.

crystals were formed. After heating for 15 more min, the crystals were filtered out from the hot solution and washed with hot EtOH (70% yield). Calc. for $C_{20}H_{14}N_4O_3Co: C, 57.29; H, 3.85; N, 13.36; Co, 14.1. Found: C, 56.73; H, 3.88; N, 13.46; Co, 14.1%. <math>\nu_{max}^{\rm EtOH}$, (log ε): 45.5, (4.6); 39.4, (4.6); 32.8, (4.4); 27.4, (4.3); 18.4, (4.2). $\mu_{\rm eff}/BM: 4.20$. The zinc complex was similarly obtained as dark red needles (70% yield). Calc. for $C_{20}H_{14}N_4O_3Zn: C, 56.43;$ H, 3.79; N, 13.16; Zn, 15.4. Found: C, 56.83; H, 3.87; N, 12.98; Zn, 15.3%. $\nu_{\rm max}^{\rm EtOH}$, (log ϵ): 45.7, (4.6); 39.8, (4.2); 32.7, (4.3); 27.6, (4.4); 18.5, (4.3). Diamagnetic.

[Fe dss Cl]: Using a solution of FeCl₂ · H₂O instead of that of CoCl₂, the Fe(III) complex was obtained as dark green flakes by the procedure similar to that for the cobalt complexes (65% yield). The Fe(III) in the starting material was aerially oxidized to Fe(III) in the complex prepared under ambient atmosphere. Calc. for $C_{18}H_8N_4O_2$ ClFe: C, 53.34; H, 2.49; N, 13.82; Fe, 14.4. Found: C, 53.86; H, 2.52; N, 13.58; Fe, 13.8%, $\nu_{\rm EOH}^{\rm EOH}$, (log ϵ): 46.1, (4.6); 38.8, (4.5); 32.3, (4.3); 27.4, (4.3); 17.9, (4.2), $\nu_{\rm eff}/BM$; 5.51.

[Mn dss] H_2O : In a three-necked 300 ml flask equipped with a dropping funnel and a reflux condenser, 0.79 g (4 mmol) of MnCl₂ $4H_2O$ were dissolved into 100 ml of EtOH under a stream of dinitrogen. Into the solution kept at 70°C a solution of damn (4 mmol) in 50 ml of EtOH and a solution of Hsal (8 mmol) in 15 ml of EtOH were successively added. The mixed solution was heated for 5 min, and then 1.5 ml of triethylamine were added to it to give dark brown needle-like crystals. After heating for 15 more min, the crystals were filtered out and washed with hot EtOH (75% yield). Calc. for $C_{18}H_{10}N_4O_2Mn$: C, 55.82; H, 3.12; N, 14.47; Mn, 14.2. Found 56.22; H, 3.08; N, 14.28; Mn, 14.0%. The complex was decomposed in solution under ambient atmosphere. μ_{eff}/BM : 5.86.

By similar procedure it was tried to prepare an Fe(II) complex. The product, dark brown needles, however, has not yet been characterized with reproducible results of analysis and several observations.

RESULTS AND DISCUSSION

The general preparative scheme for the formation of these metal complexes is described as the template reactions as follows:

$$MCl + damn + 2Hsal \xrightarrow{\text{in EtOH}} [M dss] + 2H_2O + 2HCl$$

$$(M = Cu, Ni, Pd) \qquad (i)$$

 $[M dss] \cdot C_2H_5OH + 2H_2O + 2HCI$ (M = Co, Zn) (ii)

$$[M dss] \cdot H_2O + H_2O + 2HCl \quad (M = Mn)$$
(iii)

 $[Fe^{III}dss Cl] + 2H_2O + HCl + H^+ + e^-.$ (M = Fe) (iv)

When the solution is cooled down, yellow needles of Hds are mixed with the product; the formation of Hds appears to be competitive with that of the metal-dss complex. Therefore, the product should be filtered out from the hot solution and washed with hot EtOH until the yellow tint of Hds dissappears in the filtrate. Recrystallization is usually ineffective to purify the products because of their low solubilities in common organic solvents. When the product was heated in the solution for too long duration, it occasionally decomposed to Hds and the metal chloride, or polymerized into non-stoichiometric substances.

The diamagnetism of [Ni dss] and [Pd dss] indicates that both the d^8 metal ions are in the low-spin states, taking the square-planar configuration as well as that suggested for [Cu dss][6]. On the other hand, the effective magnetic moments of Co(II), Mn(II) and Fe(II) in the respective complexes show the values for the high-spin states of these metal ions. The electronic spectra measured in EtOH, however, did not provide any convincing informations to discuss either their coordination structures or the electronic states of the central metal ions. The strong absorption maxima with log ϵ values larger than 4 are attributable to the charge transfer bands and/or to the electronic transitions in the unsaturated ligand molecule.

The temperature dependency of magnetic susceptibility was observed for [Cu dss] and [Fe dss Cl]. Both the complexes obey Curie's law down to 6 K. These complexes appear not to have any anomalous magnetic interactions such as those observed for [Cu salen][8] and [Fe salen Cl][9].

The IR and Raman spectra of the prepared complexes showed the general features similar to each other except the detail being discussed later. We did have the difficulty in observing Raman spectra for both the solution and the solid samples. Since the solubilities are low, ca. 0.5 mmol/dm³ solutions in benzene or acetone were sealed into glass capillaries as the solution samples. Lower laser power levels had to be applied for both the exciting lines at 488.0 and 514.5 nm to avoid boiling of the solution and decomposition of the complex. Therefore, we could not observe polarization behavior of the Raman bands with satisfiable precisions. For the solid samples, high laser power levels also caused decomposition even using the rotating holder. The spectra observed for the solution and the solid samples showed the wave numbers and the trend in intensity similar to each other for the respective complex with both the exciting lines except those Raman bands of the wave numbers lower than 500 cm⁻¹. There appeared a very strong and broad (probably fluorescent) band in 400- 300 cm^{-1} region, the band which varied its shape and intensity from sample to sample of the same complex. A typical example of the Raman spectra is shown in Fig. 1. Reproducible results observed in 500-1650 cm⁻¹ region are listed in Table 1 along with the IR bands observed in 1100–1650 cm^{-1} region for the sake of comparison.

As Table 1 shows, for the Cu(II), the Ni(II) and the Pd(II) complexes, the medium to strong Raman bands at 1561, 1571, and 1564 cm^{-1} , respectively, have the IR counterparts at the wave numbers within the experimental errors $\Delta \nu = 6 \text{ cm}^{-1}$. The corresponding Raman bands for the Co(II), the Zn, the Mn(II), and the Fe(III) complexes appear at 1554, 1553, 1550 cm⁻¹, and 1563 cm⁻¹, respectively, without IR counterparts; these wave numbers are lower by ca. 10 cm⁻¹ than those for the former complexes except for the Fe(III) complex. Although we have not yet had any definite structural informations about these complexes, we can suppose that the Raman band in the 1570-1550 cm⁻¹ region is "structure-sensitive". Felton et al. [10, 11] suggested that a Raman band at *ca.* 1590 cm^{-1} observed for several metalloporphyrins is structure-sensitive based on the discussion about the shift of this band in relation to the displacement of central metals from the plane of the macrocylic ligands. The present dss^{2-} is not a fused ring with rigid planarity but more flexible against central metal ions. The former group, i.e. [Cu dss], [Ni dss] and [Pd dss], can be seen to have planar structures; the characteristic coincidence between Raman and IR bands can be interpreted in terms of the C_{2v} symmetry of these complex molecules. On the other hand it is quite difficult to interpret the appearance of Raman band alone for the latter group of complexes. However, it is reasonable to suppose "distorted" structures for the Co(II) and the Zn(II) complexes because of

Raman		1	[]]]	511	dss]		001~2"5"	5 1171 -	881c245/24		00-1-00 		С. р с Р
	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IK	Kaman	н Н	катап	¥
1613s	1610s	1620m	1616s		1618s		1613s		1618s			1 to 1 2 m	1608s
				1611w	1610s	1607m	1607s	1611m	1608s	1605s	1607s		
	1576s		1581s		1584s		1576s		1584s		1582s		1575s
1561s	1563s	1571s	1569s	1564m	1569s	1154m		1553m		1550m		1563s	
15205	15155	1 El 7 W	isîre	1514w	1515s	1520m	1515s	152.8w	1524s	1524s	1528s	1.528m	15265
1463m	1461m	1462w	1465s	1462w	1460s	1456w	1458s	1466m		1460m	1464s	1462s	1461m
1445w	1441s				1433w	1435w	1433s	1446w	1442s	1438m	1436s	1432w	1437s
		1424s		1418w	1418m			1420m	1422m				
	1393s	1385w	1389s		1396m		1387s		1396s]402s		1391s
	13855				1380m							1383w	1384s
1367s	1374m			1368w								1362s	
						1353s		1356s		1350m	1352m		
1338w	1333w	1345s	1345s	1333w	1336w	1345w	1334m	1332vw	, 1340w				1334w
1313vw	1316w	1317w	1317w		1312w		1312m	1313vw	r 1311m		1324m	1 32 3m	
										1298w	1307m		1309m
1259m	1254w	1265m		1261w				1258w					
		1245w	1240w		1240w	1245w	1251w		1250w	1249w	1254m		1250w
1184w	1183s	1195m	11965	1180s	1182s	1180w	1178s	1180w	1185s	1182m	1177s		
1157s		1156s	1152s	L153s	1158m	1139m	1142m	1154m	1152m	1151s	1153s	1150w	1151m
1130w	1129s	1123w	1129w		1132w	1125w	1129m	1133w	1130w		1128m		1139m
1 				1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		1030vw	1						
						967vw	~						
922w		927w		a75/w		917w		918 VN	1	914w		923m	
820vw		830w	N									837w	
758w				763vw	1	750Vh	~						
		671m		651m									
631m		634w											
		603m		614m				613s				615s	
597s						605s		595s		607w		601s	
						588s		585s		587s			
565m				r, 7.6 r		550w		550s				24 L C	
		537W	×			535w				25 av			
		517w										5025	

Table 1. Raman and selected IR bands*

JINC Vol. 42, No. 3-C



Fig. 1. Raman spectrum for [Ni dss]: the exciting radiation, 514.5 nm line from Ar⁺ ion laser; intensity in arbitrary unit; the intensity scale below 400 cm⁻¹ has been multiplied by 5×10^{-2} times that above 400 cm⁻¹.

the tendency of the central metals to take tetrahedral coordination. Contribution from the fifth coordination would be taken into account for the Mn(II) and the Fe(III) complexes. Besides the band above-mentioned, a few Raman bands in Table 1 lack IR counterparts for the respective complexes. Although the problem has still been unsolved, it may be due to the resonance effect on the Raman spectra.

REFERENCES

- 1. E. G. Miles, M. B. Hursthouse and A. G. Robinson, J. Inorg. Nucl. Chem. 33, 2015 (1971).
- 2. J. W. Lauher and J. A. Ibers, Inorg. Chem. 14, 640 (1975).
- 3. F. C. Senftleber and W. E. Geiger, Jr., J. Am. Chem. Soc. 97, 5018 (1975).

- 4. F. C. Senftleber and W. E. Geiger, Jr., Inorg. Chem. 17, 3615 (1978).
- 5. P. S. Robertson and J. Vaughan, J. Am. Chem. Soc. 80, 2691 (1958).
- 6. T. Iwamoto and H. Suzuki, Chem. Lett. 343 (1976).
- 7. The measurements were done by the courtesy of Prof. Kazuko Sekizawa at Deparment of Physics, Faculty of Science and Engineering, Nihon University.
- 8. G. O. Carlisle, G. D. Simpson and W. E. Hatfield, Inorg. Nucl. Chem. Lett. 9, 1247 (1973).
- 9. M. Gerloch, J. Lewis, F. E. Mabbs and A. Richards, J. Chem. Soc. (A), 112 (1968).
- 10. R. H. Felton, N. T. Yu, D. C. O'Shea and J. A. Shelnutt, J. Am. Chem. Soc. 96, 3675 (1974). 11. L. D. Spaulding, C. C. Chang, N. T. Yu and R. H. Felton, J.
- Am. Chem. Soc. 97, 2517 (1975).