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Preparation and Characterization of Oxovanadium(IV), Acetatomanganese(III), Chloroiron(III), Nickel(II), Copper(II), Zinc(II) and Palladium(II) Complexes of 3,3'-(1,2-Phenylenediimino)diacrolein

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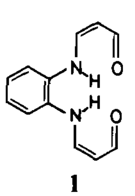
Abstract

The oxovanadium(IV), acetatomanganese(III), chloroiron(III), nickel(II), copper(II), zinc(II) and palladium(II) of 3,3'-(1,2-phenylenediimino)diacrolein were prepared and investigated by means of mass, electronic, vibrational, NMR and ESR spectroscopy as well as magnetic susceptibility measurements. The acetatomanganese(III) and chloroiron(III) complexes were confirmed to be of high spin type. The absorption bands appearing in the energy range greater than 23 000 cm^{-1} were attributed to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and charge-transfer transitions from metal to ligand. The metal complexes assume the square-planar configuration type since the ligand-field bands were detected in the 12 700–18 500 cm^{-1} region. Strong bands appearing at 1601 and 1627 cm^{-1} were assigned to the C=C and C=O stretching vibrational modes, respectively, and were shifted to lower frequency upon metal-coordination. A V=O stretching band was observed at 982 cm^{-1} for the oxovanadium(IV) complex and a C=O stretching band was observed at 1547 cm^{-1} for the acetatomanganese(III) complex. Upon complex formation the amine proton signal is found to vanish and the aldehydic methine proton signal in the lowest field is shifted upfield for the nickel(II), zinc(II) and palladium(II) complexes. ^{13}C NMR spectra support the coordination structure of the complexes which is revealed by ^{1}H NMR spectra. As judged by the spin Hamiltonian parameters, the oxovanadium(IV) complex is of a square-planar type with an unpaired electron in the d_{xy} orbital and the copper(II) complex assumes a distorted square-planar coordination due to the presence of five- and six-membered chelate rings with an unpaired electron in the $d_{x^2-y^2}$ orbital.

Introduction

Though the chemistry of Schiff base complexes prepared from salicylaldehyde or 2,4-pentanedione and 1,2-ethanediamine or 1,2-diaminobenzene has been extensively investigated up to the present time [1], examples of Schiff base complexes derived from 1,2-diaminobenzene and 2-propynal are rare. Hiller *et al.* [2] and Mueller and Woehrle [3] reported the synthesis of nickel(II) and copper(II) complexes with 3,3'-(1,2-phenylenediimino)diacrolein prepared from 1,2-diaminobenzene and 2-propynal as an intermediate to produce the desired 5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine without the work of magnetic and optical properties.

In the present study, we employed seven metal complexes of 3,3'-(1,2-phenylenediimino)diacrolein (**1**); oxo{3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}vanadium(IV) (**1**-VO), acetato{3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}manganese(III) (**1**-MnOCOCH$_3$), chloro{3,3'-(1,3-phenylenedinitrilo)dipropionaldehydato}iron(III) (**1**-FeCl), {3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}nickel(II) (**1**-Ni), {3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}copper(II) (**1**-Cu), {3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}zinc(II) (**1**-Zn) and {3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}palladium(II) (**1**-Pd). We report the results of electronic spectra for the oxovanadium(IV), acetato-



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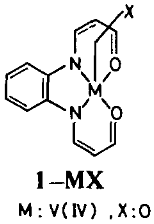
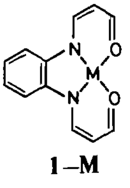


1–MX

M : V(IV) , X : O
M : Mn(III), X : OCOCH$_3$
M : Fe(III), X : Cl



1–M

M : Ni(II), Cu(II),
Zn(II), Pd(II)

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manganese(III), chloroiron(III), nickel(II), copper(II), zinc(II) and palladium(II) complexes as well as infrared spectra of the complexes. The detailed ^{1}H and ^{13}C NMR research for the nickel(II), zinc(II) and palladium(II) complexes, the magnetic susceptibility for the acetatomanganese(III), chloroiron(III) and nickel(II) complexes and the ESR data for the oxovanadium(IV) and copper(II) complexes are also provided.

Experimental

Physical Measurements

Electron impact mass spectra (at 70 eV) for Schiff base ligand (**1**) and its oxovanadium(IV), chloroiron(III), nickel(II), copper(II), zinc(II) and palladium(II) complexes and field desorption mass spectra (at 20–30 mA) for its chloroiron(III) and acetatomanganese(III) complexes were carried out with a JEOL JMS-DX 300 gas chromatograph–mass spectrometer. Magnetic susceptibility measurements were done on solid powdered samples at room temperature by using standard Faraday balance techniques with $[Ni(en)_3]S_2O_3$* as a calibrant. Diamagnetic corrections were made with the use of Pascal's constants. Ultraviolet and visible spectra covering the 11 500–50 000 cm^{-1} region were taken on a Shimadzu UV-200S double beam spectrophotometer for methanol solutions at room temperature. Infrared spectra in the range of 400–4000 cm^{-1} were measured with a JASCO IRA-2 grating spectrophotometer at room temperature by a KBr disk method. ^{1}H and ^{13}C NMR spectra were recorded in the pulsed Fourier transform mode on a JEOL JNM-FX 60 spectrometer. The NMR spectra were run in dimethyl sulfoxide-d$_6$ (D > 99.8; E. Merck, Darmstadt) or chloroform-d (D > 99.8; Aldrich Chemical Co.) and chemical shifts are reported in ppm relative to tetramethylsilane as an internal reference standard. ESR spectra were obtained at room temperature on a JEOL JES-ME-1 X-band spectrometer equipped with a 100 kHz field modulation unit. The oxovanadium(IV) and copper(II) complexes of Schiff base were doped in (≃1 wt.%) the corresponding isomorphous nickel(II) complex for measurements. All the ESR sensitive metal complexes were also measured in xylene–benzene (2:1 *v*/*v*) at room temperature. The manganese ion diffused into magnesium oxide was used to obtain the standard reference signals for measurements.

Preparation of the Ligand

3,3'-(1,2-phenylenediimino)diacrolein (1)

This was prepared after Hiller *et al.* [2] from 1,2-diaminobenzene (19.6 g) and 2-propynal (24.5 g) [4] in methanol (290 ml). The crystalline solid was recrystallized from chloroform to give pale yellow prisms; yield 14.6 g (37%), melting point (m.p.) 166.0–167.0 °C (dec) (lit., [2], yield 16%, m.p. 163–165 °C). *Anal.* Found: C, 66.06; H, 5.60; N, 12.77%; M$^+$, 216. Calc. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96%; M, 216.24.

Preparation of the Complexes

Oxo{3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}vanadium(IV) (1-VO)

A mixture of **1** (0.20 g) and *N,N*-dimethylformamide (3 ml) was added to vanadium(IV) chloride oxide (0.40 g) which was dissolved in methanol (3 ml) and heated at 50 °C for 30 min with stirring. To the filtrate of the hot mixture was added water (300 ml). Upon cooling the mixture in a refrigerator overnight, the crystalline product was recrystallized from *N,N*-dimethylformamide to give brown needles; yield 0.07 g (18%), m.p. >300 °C. *Anal.* Found: C, 51.72; H, 3.87; N, 10.02%; M$^+$, 281. Calc. for $C_{12}H_{10}N_2O_3V$: C, 51.26; H, 3.59; N, 9.96%; M, 281.16.

Acetato{3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}manganese(III) (1-MnOCOCH$_3$)

A mixture of **1** (0.10 g) and *N,N*-dimethylformamide (3 ml) was added to manganese(II) acetate tetrahydrate (0.17 g) which was dissolved in methanol (1.5 ml) and heated at 50 °C for 30 min with stirring. After the mixture was cooled down with ice-water, the crystalline solid was separated and washed three times with methanol (0.5 ml) to give green needles; yield 0.09 g (59%), m.p. >300 °C. *Anal.* Found: C, 51.04; H, 4.06; N, 8.56; Mn*, 16.9%; M$^+$, 328. Calc. for $C_{14}H_{13}N_2O_4Mn$: C, 51.23; H, 3.99; N, 8.54; Mn, 16.74%; M, 328.20.

Chloro{3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}iron(III) (1-FeCl)

A mixture of **1** (0.15 g) and *N,N*-dimethylformamide (3 ml) was added to hydrated iron(II) chloride (0.15 g) which was dissolved in methanol (3 ml) and heated at 50 °C for 30 min while air was continuously bubbled through it. After being allowed to stand overnight at room temperature, the crystalline product was recovered and washed three times with methanol (1 ml) to give dark blue needles; yield 0.11 g (52%), m.p. >300 °C. *Anal.* Found: C, 47.16; H, 3.38; N, 9.21%; M$^+$, 305. Calc. for $C_{12}H_{10}N_2O_2ClFe$: C, 47.18; H, 3.30; N, 9.17%; M, 305.52.

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*en = 1,2-ethanediamine.

*The chelating reagent (ethylenediamine-*N,N,N',N'*-tetraacetic acid) was used for the manganese analysis.

{3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}nickel(II) (1-Ni)

This complex was prepared from nickel(II) acetate tetrahydrate (0.86 g) and **1** (0.50 g) in a mixed solvent composed of methanol (5 ml) and *N,N*-dimethylformamide (10 ml) after Hiller *et al.* [2] and recrystallized from benzene to give glittering red needles; yield 0.57 g (90%), m.p. 182.0–183.0 °C (dec) (lit., [2], yield 84%, m.p. 165–167 °C). *Anal.* Found: C, 53.14; H, 3.57; N, 10.23%; M^+, 272. Calc. for $C_{12}H_{10}N_2O_2Ni$: C, 52.80; H, 3.70; N, 10.27%; M, 272.91.

{3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}copper(II) (1-Cu)

Prepared from copper(II) acetate monohydrate (0.69 g) and **1** (0.50 g) in a mixed solvent composed of methanol (5 ml) and *N,N*-dimethylformamide (10 ml) after Hiller *et al.* [2]. The product was recrystallized from benzene as glittering dark brown needles; yield 0.57 g (89%), m.p. 203.0–205.0 °C (dec) (lit., [2], yield 92%, m.p. 203–205 °C). *Anal.* Found: C, 52.21; H, 4.18; N, 10.08%; M^+, 277. Calc. for $C_{12}H_{10}N_2O_2Cu$: C, 51.89; H, 3.63; N, 10.09%; M, 277.77.

{3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}zinc(II) (1-Zn)

A mixture of **1** (0.12 g) and *N,N*-dimethylformamide (2 ml) was added to zinc(II) acetate dihydrate (0.15 g) which was dissolved in methanol (3 ml) and heated at 45 °C for 1 h with stirring. After addition of acetone (6 ml), the reaction mixture was allowed to stand overnight at room temperature. The crystalline product was separated and washed twice with acetone (2 ml) to give yellow needles; yield 0.10 g (64%), m.p. >300 °C. *Anal.* Found: C, 45.32; H, 3.73; N, 7.47; Zn*, 26.7%. Calc. for $C_{12}H_{10}N_2O_2Zn \cdot 0.5Zn(C_2H_3O_2)_2$: C, 45.28; H, 3.53; N, 7.54; Zn, 27.30%.

{3,3'-(1,2-phenylenedinitrilo)dipropionaldehydato}palladium(II) (1-Pd)

A mixture of **1** (0.20 g) and *N,N*-dimethylformamide (2 ml) was added to palladium(II) acetate (0.22 g) which was dissolved in methanol (4 ml) and heated at 50 °C for 1 h with stirring. After being cooled with ice-water, water (50 ml) was added to the reaction mixture. The precipitates were recovered and extracted with chloroform (100 ml). After the extractant was evaporated off *in vacuo*, the chloroform solution of this residue was applied to the top of a chromatographic column of silica gel (60–80 mesh, Kanto Chemical Co., Inc.) and eluted with chloroform. The initial effluent was concentrated *in vacuo* and the product was separated as yellow pillar-like crystals; yield 0.26 g (88%), m.p. 202.5–204.0 °C (dec). *Anal.* Found: C, 44.76; H, 3.33; N, 8.76%; M^+, 320. Calc. for $C_{12}H_{10}N_2O_2Pd$: C, 44.95; H, 3.14; N, 8.74%; M. 320.62.

Results and Discussion

Magnetic Susceptibilities

The results of magnetic susceptibility measurements for the acetatomanganese(III) (**1**-$MnOCOCH_3$), chloroiron(III) (**1**-FeCl) and nickel(II) (**1**-Ni) complexes are summarized in Table I together with those for salen-$MnOCOCH_3$ [5], **2**-MnNCS [6], salen-FeCl [7], **3**-FeCl [8] and **3**-Ni [8] complexes. It can be seen that **1**-$MnOCOCH_3$ as well as **1**-FeCl contains a spin-free state and **1**-Ni holds a diamagnetism. The effective magnetic moments for **1**-$MnOCOCH_3$ and **1**-FeCl indicate that the nuclear manganese and iron have oxidation states of +3 in each case and are in fair agreement with spin-only values and those reported for **2**-MnNCS and salen-FeCl complexes, respectively.

TABLE I. Magnetic Susceptibility Results for Schiff Base Complexes

Complex[a]	Electronic configuration	Temperature (K)	μ_{eff}[b] (BM)	$[4S(S+1)]^{1/2}$ (BM)	No. of unpaired electrons	Reference
1-$MnOCOCH_3$	4	296.5	4.84	4.90	4	this work
salen-$MnOCOCH_3$	4	300.8	4.68	4.90	4	5
2-MnNCS	4	296.0	4.89	4.90	4	6
1-FeCl	5	296.9	5.93	5.92	5	this work
salen-FeCl	5	295.0	5.90	5.92	5	7
3-FeCl	5	298.5	3.85	3.87	3	8
1-Ni	8	297.0	dia.	0	0	this work
3-Ni	8	298.5	dia.	0	0	8

[a] **1** = 3,3'-(1,2-Phenylenediimino)diacrolein; salen = *N,N'*-ethylenebis(salicylideneimine); **2** = 5,14-dihydro-2,3,11,12-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine; **3** = 5,14-dihydro-7,16-diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine. [b] Dia = diamagnetism.

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*The chelating reagent (ethlenediamine-*N,N,N',N'*-tetraacetic acid) was used for the zinc analysis.

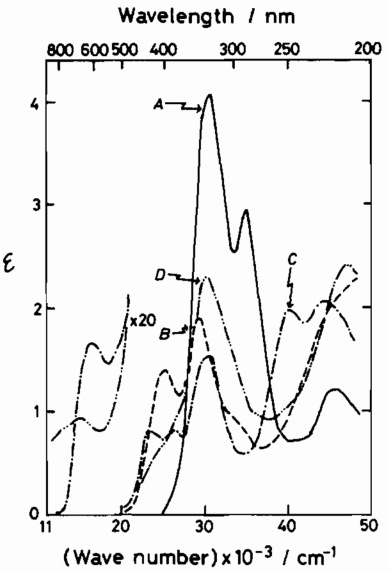


Fig. 1. Electronic absorption spectra for 3,3′-(1,2-phenylenediimino)diacrolein chelates in methanol at room temperature. A, Ligand; B, oxovanadium(IV); C, acetatomanganese(III); D, chloroiron(III).

Mass Spectra

The field desorption (FD) mass spectra for 1-MnOCOCH$_3$ and 1-FeCl complexes establish the presence of a molecular ion M$^+$ at m/z 328 and 305, respectively, as described in 'Experimental'. Using the electron impact (EI) mass spectrum, the masses of the major fragment at m/z 269 and 270 correspond to [M – OCOCH$_3$]$^+$ and [M – Cl]$^+$, respectively, and these fragment peaks are the base peaks in the mass spectrum.

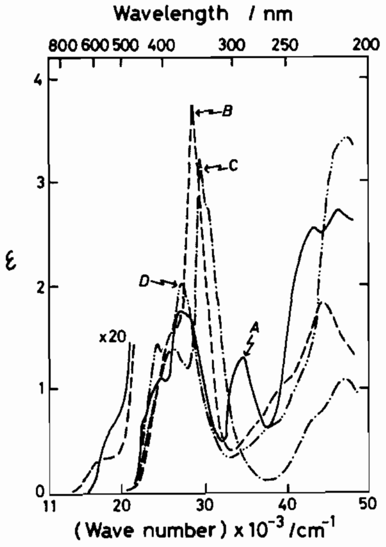


Fig. 2. Electronic absorption spectra for 3,3′-(1,2-phenylenediimino)diacrolein chelates in methanol at room temperature. A, Nickel(II); B, copper(II); C, zinc(II); D, palladium(II).

Electronic Spectra

The electronic spectra covering the 11 500–48 000 cm^{-1} region are shown in Fig. 1 for the oxovanadium(IV), acetatomanganese(III) and chloroiron(III) complexes and in Fig. 2 for the nickel(II), copper(II), zinc(II) and palladium(II) complexes of 3,3′-(1,2-phenylenediimino)diacrolein (1). The ab-

TABLE II. Electronic Absorption Bands for Schiff Base Complexes

Complex[a]	Transition energy in cm^{-1} (ϵ)[b]		
	d → d*	π → π*/charge-transfer	
1		30600(40700)	35000(29300)
		45700(12300)	
1-VO	13300sh(26)	25190(14000)	29200(19200)
		33800sh(9000)	44600sh(19300)
1-MnOCOCH$_3$	16400(834)	23300(8240)	26300(8270)
		30500(15500)	40200(19800)
		44300(20800)	
1-FeCl	12700sh(418)	29900(23100)	47000(24100)
	15000(476)		
1-Ni	18500sh(300)	24900(11000)	27200(17600)
		34800(13000)	43500(25500)
		46300(27200)	
1-Cu	17000sh(154)	25800sh(15100)	28700(37500)
		39400sh(10300)	44600(18300)
1-Zn		26200(14000)	29500(32200)
		30500sh(27400)	42900sh(6960)
1-Pd		24400(14300)	27500(20400)
		37000sh(5900)	47600(34400)

[a] See Table I for numbering of the ligand 1. [b] Measured in methanol at room temperature.

sorption bands appearing in the energy range greater than 23 000 cm^{-1} are reasonably attributed to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and charge-transfer transitions from metal to ligand, because the molar extinction coefficients of these bands ($\sim 10^4$ mol^{-1} dm^3 cm^{-1}) are much larger than those normally assigned to ligand-field transitions [9]. The $\pi \rightarrow \pi^*$ and/or charge-transfer transition energies for the metal chelates are summarized together in Table II.

The absorption bands observed in the lower energy scope up to 18 500 cm^{-1} are attributable to $d \rightarrow d^*$ transitions of the metal atoms as judged by the molar extinction coefficients of these bands ($10 \sim 10^2$ mol^{-1} dm^3 cm^{-1}), as listed in Table II. The nickel(II) and palladium(II) complexes do not show any significant absorption in the region lying below 15 000 cm^{-1}. This spectral behavior is consistent with the square-planar coordination of nickel(II) and palladium(II). Owing to the presence of intense $\pi \rightarrow \pi^*$ and/or charge-transfer absorption bands in the higher energy range, we failed to observe ligand-field bands for the palladium(II) complex.

The copper complex demonstrates a weak absorption band at about 17 000 cm^{-1} which is due to the $d \rightarrow d^*$ transition of the metal atom. When the copper atom is placed in the square-planar ligand-field, a $d \rightarrow d^*$ absorption band has been known to appear in the 14 300–20 000 cm^{-1} region [9]. Consequently, the copper atom in 3,3'-(1,2-phenylenediimino)diacrolein complex attains primarily the square-planar coordination.

The general features of the spectra for the oxovanadium(IV), acetatomanganese(III) and chloroiron(III) complexes are analogous to those observed for the typical five coordinate complexes of C_{4v} symmetry [9]. These metal complexes assume square-pyramid configurations.

The zinc(II) complex shows four absorption bands in the 26 000–43 000 cm^{-1} range. In the absence of the $d \rightarrow d^*$ origin, these bands are considered to be due to the $\pi \rightarrow \pi^*$ and/or charge-transfer transitions.

Vibrational Spectra

The characteristic IR absorption bands, which are meaningful for the present discussion, are collected in Table III for metal-free 3,3'-(1,2-phenylenediimino)diacrolein and its complexes along with those for copper(II) and palladium(II) complexes of 2,4-pentanedione. The present metal-free ligand exhibits a gentle band at 3200 cm^{-1} which is correlated with an N–H stretching mode. This vibrational mode fades out upon complex formation.

Strong absorption bands observed at 1601 and 1627 cm^{-1} can be attributed to the stretching mode of C=C and C=O bonds, respectively, in a manner

TABLE III. Characteristic IR Absorption Bands for Schiff Base Complexes[a], [b]

Ligand[c]	Metal	IR band (cm^{-1})	Assignment	Reference
1		1601(s)	ν(C=C)	
		1627(s)	ν(C=O)	
		3200(w)	ν(N–H)	
1	V(IV)O	982(m)	ν(V=O)	
		1583(s)	ν(C=O)	
		1593(s)	ν(C=C)	
1	Mn(III)OCOCH$_3$	1547(s)	ν(C=O)(acetato)	
		1579(s)	ν(C=O)	
		1594(s)	ν(C=C)	
1	Fe(III)Cl	1578(s)	ν(C=O)	
		1590(s)	ν(C=C)	
1	Ni(II)	1584(s)	ν(C=O)	
		1595(s)	ν(C=C)	
1	Cu(II)	1585(s)	ν(C=O)	
		1596(s)	ν(C=C)	
1	Zn(II)	1565(s)	ν(C=O)(acetato)[e]	
		1585(s)	ν(C=O)	
		1599(s)	ν(C=C)	
1	Pd(II)	1587(s)	ν(C=O)	
		1595(s)	ν(C=C)	
4[d]	Cu(II)	1552(s)	ν(C=O)	10
		1577(s)	ν(C=C)	
4	Pd(II)	1549(s)	ν(C=O)	10
		1569(s)	ν(C=C)	

[a] Measured by KBr disk method at room temperature. [b] Relative intensities; s, strong; m, medium; w, weak. [c] See Table I for numbering of the ligand 1. [d] 2,4-Pentanedione. [e] Owing to containing a Zn(OCOCH$_3$)$_2$.

TABLE IV. ^{1}H NMR Data for Schiff Base Complexes[a]

Sample	Amine –N–H	Aromatic	Methine		
			O=C$\underline{H}$–CH=	–CH=C$\underline{H}$–NH–	–C$\underline{H}$=CH–NH–
Ligand	9.38(d) (J = 12.1 Hz)	7.4–7.0(m)	9.21(d) (J = 8.6 Hz)	7.81(dd) (J = 12.8 Hz) (J = 12.1 Hz)	5.52(dd) (J = 12.8 Hz) (J = 8.6 Hz)
Ni-chelate		8.0–6.9(m)	7.93(d) (J = 6.2 Hz)	7.40(d) (J = 4.0 Hz)	5.65(dd) (J = 6.2 Hz) (J = 4.0 Hz)
Zn-chelate[b]		7.6–6.9(m)	8.19(d) (J = 5.4 Hz)	8.20(d) (J = 4.5 Hz)	5.03(dd) (J = 5.4 Hz) (J = 4.5 Hz)
Pd-chelate		8.1–7.0(m)	8.24(d) (J = 6.5 Hz)	7.81(d) (J = 4.4 Hz)	5.56(dd) (J = 6.5 Hz) (J = 4.4 Hz)

[a] Chemical shifts are given in ppm for TMS. Measured in dimethyl sulfoxide-d_6. Multiplicity of a proton signal is given in parentheses after δ value; d = doublet, m = multiplet, dd = doublet of doublets. [b] The methyl proton peak of $Zn(OCOCH_3)_2$ appears at 1.81 ppm.

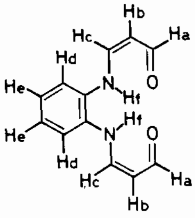
as observed for the metal-free 2,4-pentanedione [10]. These bands are most sensitive to metal-coordination among the absorption peaks appearing in the usual infrared range and shift greatly to lower frequency upon metal-coordination, respectively. Such a spectral behavior has been obtained for 2,4-pentanedione complexes [10].

A medium absorption band at 982 cm^{-1} observed for the oxovanadium(IV) complex is attributed to the V=O stretching vibrational mode since a similar spectral feature has been observed for the oxo(2,4-pentanedionato)(pyridine)vanadium(IV) complex [10] and no band in this region was detected for the other metal complexes.

A strong absorption peak in the 1547–1565 cm^{-1} range was observed for the manganese(III) and zinc(II) complexes and attributable to the C=O stretching vibrational mode of the acetate ion [10]. Judging from the C=O stretching frequency the acetate group for the manganese complex may be present not as a simple isolated ion but as a coordinated group [10]. On the other hand, a strong absorption band observed at 1565 cm^{-1} for the zinc(II) complex, that is, $(1\text{-}Zn)\cdot 0.5Zn(OCOCH_3)_2$ is attributed to the C=O stretching vibrational mode of the acetate group caused by zinc(II) acetate involved in the crystal lattice.

NMR Spectra

^{1}H NMR data and their assignments for 3,3′-(1,2-phenylenediimino)diacrolein and its metal complexes are compiled in Table IV. The H_f-amine proton shown by 2 couples with the H_c-methine proton and the H_f-signal is split into a doublet. The H_a-methine proton couples with the H_b-methine proton, the H_a-signal being split into a doublet.



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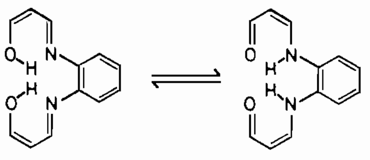


3

The H_b-methine proton couples with both H_a- and H_c-methine protons, the H_b-signal being split into a doublet of doublets, which was observed as a quartet. The H_c-methine proton couples with both the H_b-methine and H_f-amine protons and the H_c-signal is split into a doublet of doublets in analogy with the H_b-methine proton. It can be assumed that there are two possible tautomeric structures shown by 3, but there is no tautomeric effect as judged by infrared and NMR data as mentioned before.

The signal (9.38 ppm) for the H_f-amine proton was found to vanish upon metal-coordination. An analogous spectral change was observed upon substitution of the H_f-proton on the nitrogen with deuterium (D) in the metal-free ligand. The H_a-methine proton peak (9.21 ppm) observed for the metal-free ligand in the lowest field is shifted upfield

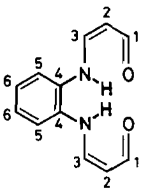
TABLE V. ^{13}C NMR Data for Schiff Base Complexes[a]

Sample	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
Ligand[b]	189.0(2)	106.2(2)	153.1(2)	131.5(1)	120.0(2)	124.5(2)
Ni-chelate[c]	171.3(2)	98.9(2)	146.8(2)	142.2(1)	113.5(2)	124.8(2)
Zn-chelate[b]	177.1(2)	97.5(2)	154.8(2)	138.8(1)	114.4(2)	124.3(2)
Pd-chelate[b]	171.5(2)	98.0(2)	145.8(2)	142.1(1)	115.1(2)	125.4(2)

[a] Chemical shifts are given in ppm for TMS. Multiplicity of an off resonance signal is given in parentheses after δ-value. [b] Measured in dimethyl sulfoxide-d_6 with TMS as an internal reference. [c] Measured in chloroform-d with TMS as an internal reference.

by 0.97 (palladium complex), 1.02 (zinc complex) and/or 1.28 ppm (nickel complex) upon complex formation. This may be attributed to a decrease of the ring current by combination of the nickel, zinc and/or palladium. The shielding effect by nickel(II)-coordination is larger than that by palladium(II)-coordination. Upon complex formation the H_c-methine proton signal turned out to be a doublet. The H_c-signal for the nickel(II) complex is shifted upfield by 0.41 ppm. The H_c-signal for the palladium(II) complex is not shifted. On the other hand, the H_c-signal for the zinc(II) complex is shifted downfield by 0.39 ppm. The H_b-methine proton signal for the nickel(II) and palladium(II) complexes is shifted downfield by 0.04 (palladium complex)–0.13 ppm (nickel complex) upon metal-coordination. This downfield shift is comparable to that observed for the Schiff base complexes [11]. On the contrary the H_b-methine proton signal for the zinc(II) complex is shifted upfield by 0.49 ppm. This upfield shift is comparable to that observed for the *meso*-methine protons of metal porphyrin [12]. This seems to indicate that the coordination structure for the zinc(II) complex is different from those for the nickel(II) and palladium(II) complexes. Furthermore, the methyl proton peak of $Zn(OCOCH_3)_2$ appears at 1.81 ppm since the zinc(II) complex contains the zinc(II) acetate in the crystal lattice. The proton signals for the aromatic group show the downfield shift upon metal-coordination. These downfield shifts can be attributed to the de-shielding effect provided by the positive charge on the metal.

^{13}C NMR data and their assignments for the ligand and its complexes are given in Table V. The C(1) olefin carbon signal (189.0 ppm) observed for the metal-free ligand in the lowest field is shifted upfield by 11.9 (zinc complex), 17.5 (palladium complex) and/or 17.7 ppm (nickel complex) upon complex formation. The C(2) olefin carbon peak (106.2 ppm) for the metal-free ligand in the highest field is also shifted upfield by 7.3 (nickel complex), 8.2 (palladium complex) and/or 8.7 ppm (zinc complex) similarly to the C(1) olefin carbon. This upfield shift is comparable to those observed for cyanometallate complexes [13] and for the methyl carbon of 2,4-pentanedione complexes [14, 15]. This may be attributed to the positive charge provided by the central metal ion. Although the C(3) olefin carbon signal for the nickel(II) and palladium(II) complexes is shifted upfield by 6.3 (nickel complex) and 7.3 ppm (palladium complex), this signal for the zinc(II) complex is shifted downfield by 1.7 ppm. The C(4) aromatic carbon signal for all metal complexes is shifted downfield by 7.3 (zinc complex), 10.6 (palladium complex) and/or 10.7 ppm (nickel complex). This downfield shift is comparable to those for σ-aryl complexes such as phenyllithium and phenylmagnesium bromide [16]. The ^{13}C NMR data are fully consistent with structure **4** which is already revealed by ^1H NMR spectrum.



4

ESR Spectra

In the ESR spectrum of the oxovanadium(IV) complex determined in xylene–benzene (2:1 v/v) at room temperature, a set of eight hyperfine lines was obtained by the magnetic interaction between a vanadium nucleus ($I = 7/2$) and an unpaired electron. The general spectral feature is similar to that observed for the oxo(5,10,15,20-tetraphenylporphinato)vanadium(IV) complex [17]. The ESR spectrum of the oxovanadium(IV) complex magnetically diluted with the corresponding nickel(II) complex at room temperature is shown in Fig. 3. This spectrum consists of two sets of vanadium hyperfine lines, namely $g_{\parallel}$ and $g_{\perp}$ components. A similar spectral feature has been obtained for the complexes induced from porphyrins [17–19], phthalocyanine [20], Schiff bases [21] and tetraaza[14]annulenes [22]. The spin Hamiltonian parameters obtained in this work are almost comparable with those for these complexes taken from the

TABLE VI. Spin Hamiltonian Parameters for Oxovanadium(IV) and Copper(II) Complexes of Schiff Base[a]

Ligand[b]	Metal	Medium	$\bar{g}$	$\lvert g_0 - g_\parallel \rvert$	$\lvert g_0 - g_\perp \rvert$	$\bar{A} \times 10^4$ (cm^{-1})	$A_\parallel \times 10^4$ (cm^{-1})	$A_\perp \times 10^4$ (cm^{-1})	$A_\perp^N \times 10^4$ (cm^{-1})	Reference
1	VO	xylene–benzene	1.986			97.2				this work
1	VO	Ni(II) complex		0.046	0.007		160.0	58.6		this work
5	VO	xylene–benzene	1.989			86.1				22
5	VO	ligand (5)		0.035	0.004		150.0	52.8		22
1	Cu	xylene–benzene	2.096			89.0				this work
1	Cu	Ni(II) complex		0.188	0.052 0.025		213.0		8.6	this work
5	Cu	xylene–benzene	2.089			96.4				22
5	Cu	ligand (5)		0.128	0.033 0.010		218.0		7.3	22

[a]Measured at room temperature. Maximum possible errors: g, ±0.0005; A, $A_\parallel$, $\pm 0.5 \times 10^{-4}$ cm^{-1}; $A_\perp$, $A_\perp^N$, $\pm 0.05 \times 10^{-4}$ cm^{-1}. [b]See Table I for numbering of the ligand **1**; **5** = 5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine. [c]Concentration of the complex, $10^{-3} \sim 10^{-4}$ mol dm^{-3} (xylene – benzene; 2:1 v/v). Ni(II) complex, {3,3′-(1,2-phenylenedinitrilo)dipropionaldehydato}nickel(II).

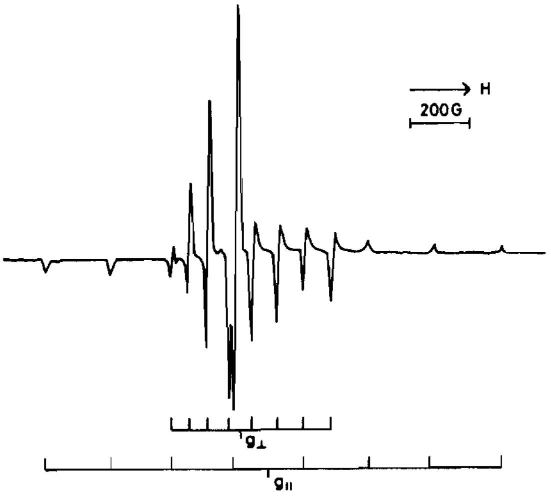


Fig. 3. ESR spectrum for oxo{3,3′-(1,2-phenylenedinitrilo)dipropionaldehydato}vanadium(IV) complex magnetically diluted with the corresponding nickel(II) complex at room temperature.

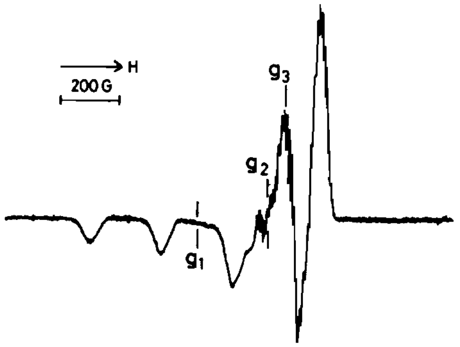


Fig. 4. ESR spectrum for {3,3′-(1,2-phenylenedinitrilo)dipropionaldehydato}copper(II) complex magnetically diluted with the corresponding nickle(II) complex at room temperature.

literature [17–22], as shown in Table VI. Accordingly, the present oxovanadium(IV) complex is of a square-planar type with an unpaired electron in the d_{xy} orbital.

Figure 4 indicates the ESR spectrum recorded at room temperature for the powdered sample of the copper(II) complex magnetically diluted with the corresponding nickel(II) complex. The general feature of the spectrum is analogous to that observed for the square-planar copper(II) complexes derived from porphyrins [17, 23] and phthalocyanine [24]. A set of four copper hyperfine lines on the $g_\parallel$ component, which lies in the low field range, is observed since such hyperfine lines on the $g_\perp$ component are not clear in the higher field range. On the other hand, the superhyperfine lines due to the nitrogen nuclei ($I = 1$) appear on the $g_\perp$ position since such superhyperfine lines do not appear on the $g_\parallel$ position. The spin Hamiltonian parameters are almost consistent with those for tetraaza[14]annulenes copper(II) complexes [22] which indicate the presence of three g values, that is, g_z, g_y, g_x. Consequently, this copper(II) complex assumes a distorted square-planar coordination due to the presence of five- and six-membered chelate rings with an unpaired electron in the $d_{x^2-y^2}$ orbital.

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