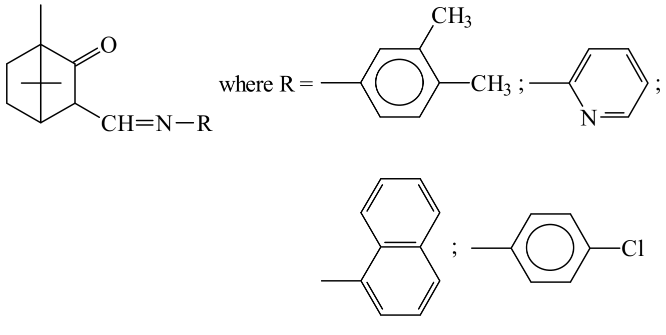
NEW COORDINATION COMPOUNDS OF Cu(II) WITH AZOMETHINE DERIVED FROM 3-FORMYLCAMPHOR AND AROMATIC AMINES. (II)

Adalgiza Ciobanu *, F. Zălaru, I. Baciu, A. Meghea, Ch. Zălaru, F. Dumitraşcu and C. Drăghici

Copper(II) complexes employing the Schiff bases derived from formylcamphor and aromatic amines as ligands have been prepared. The complex compounds $CuL_4(CH_3COO)_2$ or CuL_2 have been characterized by chemical analysis, electronic, IR, EPR spectra, differential thermal analysis. The ligands were prepared and characterized by ^1H and ^{13}C-NMR spectra.

Introduction

Our previous paper [1] has reported the synthesis and characterization of the coordination compounds of Cu(II) with Schiff bases derived from 3-formylcamphor and some aromatic amines by the type:



It has shown that these Schiff bases acted monodentately in the tautomeric form (II) by the N atom donor or by the O atom donor when the ligand has a bulky R-substituent on the N atom forming complexes compounds of the $ML_4(CH_3COO)_2$ type.

It seemed desirable to investigate the coordination ability of other Schiff bases derived from 3-formylcamphor and aromatic amines different by the number and nature of some substituents on the benzene ring. Four new ligands able to generate complexes have been synthesized and characterized by ^1H and ^{13}C-NMR spectra:

3-[(3'-nitro-phenylamino)methylene]bornan-2-one (A)

3-[(4'-nitro-phenylamino)methylene]bornan-2-one (B)

---

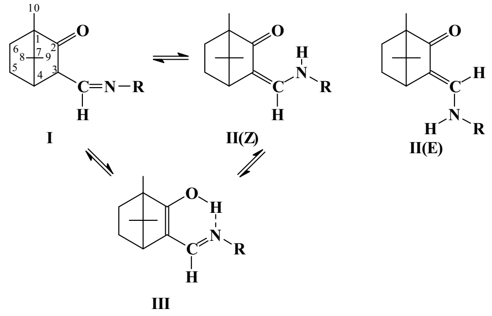
* Dept. of Organic Chemistry, Faculty of Chemistry, University of Bucharest, 90 Road Panduri, Bucharest, ROMANIA

3-[(2’-nitro-4’-methoxy-phenylamino)methylene]bornan-2-one (C)

3-[(phenylamino)methylene]bornan-2-one-4’-carboxylic acid (D)

The presence of the carbonyl and azomethine groups lying in vicinal position with respect to each favours keto-enolic-enamine tautomerism I-III (Scheme 1).

The forms (I-III) are present in tautomeric equilibrium in solid or in solution NMR-studies have shown that the tautomeric distribution was solvent dependent [2-4]. In addition, Knorr and Ruf [5] have shown by NMR studies that the nature of the R-substituent on N atom of the azomethine group brings strong differences in their tautomeric equilibrium. Also, they showed the presence of E/Z isomerism of form (II) (Scheme 1).



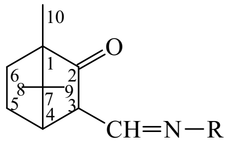
Scheme 1

Our Schiff bases (A-D) have been characterized by ^{1}H and ^{13}C-NMR spectra in $CDCl_3$ and DMSO-d_6 (Table 1).

The ^{1}H-NMR and ^{13}C-NMR spectra of free ligands put in evidence the presence of the keto-enolic-enamine tautomerism. In addition, these spectra have shown, that in DMSO-d_6 solution, the ligand (D) exists as ketoamine form (tautomer II in both Z/E diastereoisomers: >NH:9.10 (E, 85%); 9.80 (Z, 15%) and >C=O 205.3 (E); 204.4 (Z).

The ligand C due to a strong intramolecular H-bond, it exists in $CDCl_3$ solution as Z stereoisomer only. The ligands A and B exist in $CDCl_3$ solution as E stereoisomer only.

Table 1. Characteristic ^{1}H- and ^{13}C-NMR (δ ppm, J, Hz) for the ligands (A-D) in $CDCl_3$ or DMSO-d_6



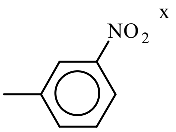
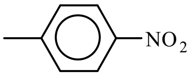
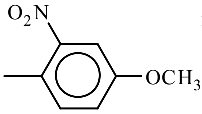
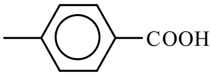
R	^{1}H-NMR	Group	^{13}C-NMR
 x NO$_2$	7.46 (d, 1H, 12.9) E	-CH=N	126.6
	7.18 (d, 1H, 12.9) E	>NH	-
	0.99, 0.97, 0.88 (3s, 9H)	10-Me, 9-Me, 8-Me	-
	-	>C=O	207.6
	-	C-10, C-9, C-8	9.3, 20.4, 18.6

Table 1. ***Continued***

R	^{1}H-NMR	Group	^{13}C-NMR
 x	7.54 (d, 1H, 13.0) E	-CH=N	125.0
	6.68 (d, 1H, 13.0) E	>NH	-
	1.00, 0.99, 0.86 (3s, 9H)	10-Me, 9-Me, 8-Me	-
	-	>C=O	207.1
	-	C-10, C-9, C-8	9.3, 20.5, 18.6
 x	6.97 (d, 1H, 11.4) Z	-CH=N	125.0
	11.91 (d, 1H, 11.4) Z	>NH	-
	1.01, 0.95, 0.85 (3s, 9H)	10-Me, 9-Me, 8-Me	-
	-	>C=O	207.9
	-	C-10, C-9, C-8	9.0, 20.6, 18.7
	-	O-Me	55.8
 xx	7.47 (d, 1H, 12.7) E = 85%	-CH=N	126.4
	7.37 (d, 1H, 12.0) Z = 15%		
	9.10 (d, 1H, 12.7) E = 85%	>NH	-
	9.80 (d, 1H, 12.0) Z = 15%		
	0.91, 0.84, 0.76 (3s, 9H)	10-Me, 9-Me, 8-Me	-
	-	>C=O	205.3 E; 204.4 Z
	-	C-10, C-9, C-8	9.5, 20.2, 18.6
	-	COOH	167.1 E; 166.9 Z

x – $CDCl_3$
xx – DMSO-d_6

Experimental

The ligands were prepared according to literature and $Cu(CH_3COO)_2.H_2O$ p.a. Merck was used. Syntheses:

1. To a warm methanolic solution (~40^{o}C) of ligand B (2 mmol.) was added a warm methanolic solution of Cu(II) acetate (1 mmol.). The microcrystalline, dark green colored, sparingly soluble, product was filtered off in vacuum and washed with methanol.

Analysis for $CuC_{72}H_{86}O_{16}N_8$: calculated: Cu, 4.60; C, 62.54; H, 6.22; found: Cu, 4.44; C, 61.81; H, 7.25

1'. To the remaining filtered light-green coloured, 10 ml of water were added and then there separated immediately a powder-form green-yellowish coloured product. This was filtered off, washed with water and air-dried.

Analysis for $CuC_{72}H_{86}O_{16}N_8$: calculated: Cu, 4.60; C, 62.54; H, 6.22; found: Cu, 4.90; C, 63.37; H, 7.19

The compounds noted 2 and 3 have been obtained following the same way as for the compound noted 1.

2. Analysis for $CuC_{76}H_{98}O_{20}N_8$: calculated: Cu, 4.22; C, 60.58; H, 6.47; found: Cu, 4.70; C, 58.16; H, 7.38

3. Analysis for $CuC_{36}H_{40}O_6N_2$: calculated: Cu, 9.63; C, 65.50; H, 6.06; found: Cu, 9.24; C, 65.21; H, 7.18

The copper contents were determined by gravimetrically analyses. The carbon, hydrogen contens were determined by microcombustion.

IR spectra (KBr, pellets) were measured on a BIO-RAD FTS-135 Spectrometer.

EPR spectra were recorded at room temperature in polycrystalline powders on ART-5-IFA Spectrograph. The clystron frequency was 9060 MHz. The EPR spectral parameters were calculated against a Mn(II) standard.

The electronic diffuse spectra within 300-1100 nm range were obtained with VSU-2P Zeiss-Jena Spectrophotometer, using MgO as a standard.

NMR spectra-all spectra were recorded on a Varian Gemini 300 Spectrometer operating at 300 MHz (^{1}H-NMR) and 75 MHz (^{13}C-NMR) respectively, in $CDCl_3$ or DMSO-d_6. The chemical shifts were referred to tetramethylsilane (TMS) as the internal standard.

Thermodifferential analyses were carried out with a Paulik-Paulik-Erdey Derivatograph Q-1500 D MOM. Conditions of measurements: temperature range at 1000^{o}C; heating program: 10 degree /min; sensivity DTA = 1/10; $m_{1'}$ = 0.0180 g; S = 20 mg and m_3 = 0.0323 g; S = 50 mg; atmosphere over sample air.

Results and Discussion

Synthesis was performed in methanolic medium in a molar ratio Cu:L = 1:2. The new complex compounds were obtained by interaction of warm methanolic ligand solution (~40^{o}C) with the methanolic Cu(II) acetate solution (40^{o}C) only with ligands B, C, D. In the same condition (molar ratio Cu:L, reaction medium), the ligand noted A did not give any complex compound.

Two different compounds having the same formula $CuB_4(CH_3COO)_2$ were obtained only with the ligand B, with the ligands C and D were obtained the compounds formulate $CuC_4(CH_3COO)_2$ and CuD_2 respectively (Table 2).

Table 2. Some physical properties

No.	Ligand	Molar ratio Cu:L	Complex	Color	M.p. (^{o}C)
1	B	1:2	$CuB_4(CH_3COO)_2$	Dark-green	162-165
1’	B	1:2	$CuB_4(CH_3COO)_2$	Green yellowish	149-152
2	C	1:2	$CuC_4(CH_3COO)_2$	Brown red	205-207
3	D	1:2	CuD_2	Light-green	270-280

All the complex compounds have been characterized by UV-VIS, IR, EPR spectra and thermodifferential analysis.

Diffuse reflectance electronic spectra of the complex compounds (Table 3) present one broad absorption band with λ_{max} different centered within 600-800 nm range which was assigned to a d-d transition expected for Cu(II) complex compounds in a distorted tetragonal octahedron with various degrees of axial distortion. It is known that this band expected within the 550-700 nm range is shifted towards the near UV range when the Cu(II) ion is in a distorted octahedron towards square-planar or it is shifted towards the IR range when the Cu(II) ion is in a compressed tetrahedral [6÷8]. In addition, the spectrum of the $CuC_4(CH_3COO)_2$ compound presents another band, too, (λ_{max} = 500 nm) which is due to the ligand C, red coloured.

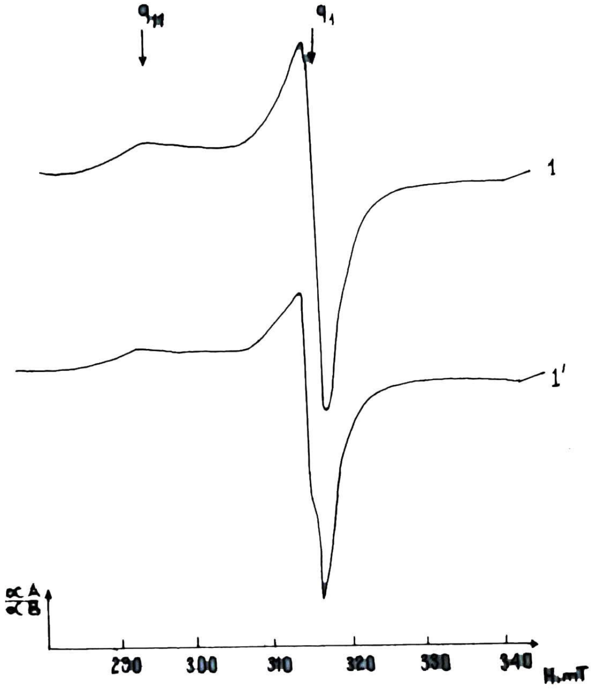


Fig. 1: *EPR spectra of the compounds 1 and 1'.*

The EPR spectra recorded at room temperature on polycrystalline samples present EPR signals characteristic of a monomeric species of Cu(II) with various degrees of axial distortion for complex compounds noted 1 and 1' only (Table 3 and Fig. 1). The shape of the line is in agreement with the geometry of the elongated axial octahedron with $g_{\|} > g_{\perp}$ for the compound noted 1. EPR signal of the compound 1' has a third order anisotropy for the factor g. This anisotropy is compatible with Cu(II) ion in a rhombic distorted geometry, axial elongated [6÷8] with R < 1 and supports the electronic spectra. In a three g value spectrum with $g_1 < g_2 < g_3$, the value of $R = (g_2 - g_1)/(g_3 - g_2)$ may be significant [6, 7]: if R > 1, a predominant d_{z^2} ground state is present and would be consistent with compressed axial or rhombic symmetry with slight misalignment of the axes; if R < 1 a predominant $d_{x^2-y^2}$ ground state is present.

Table 3. Electronic spectral data and EPR spectral parameters

No.	Complex	λ_{max} (nm)	$g_{\|} = g_3$	$g_{\perp} = g_2$	g_1
1	$CuB_4(CH_3COO)_2$	620	2.2322	2.0745	-
1'	$CuB_4(CH_3COO)_2$	560, 700sh	2.2289	2.0720	2.0550
2	$CuC_4(CH_3COO)_2$	500, 670	-	-	-
3	CuD_2	750	-	-	-

Thermodifferential analysis curves for the complex compounds by $CuL_4(CH_3COO)_2$ type are similar. Fig. 2 shows in detail thermodifferential curve for the compound noted 1'. The results indicate that the compound is stable up to 200°C, but rapidly loses ligands up to 375°C, weight loss at 375°C found: 49.88%, calculated for $2(B.CH_3COO)$ = 51.66%, the weight loss continues up to 575°C (residue (CuO) found 4.04%; calculated 5.75%). The thermal decomposition of the compound noted 3 (CuD_2) is a complex one. The analysis of the thermal curve (Fig. 3) reveals that within 20÷250°C range the ATD curve presents a weak exothermic effect without weight loss. The mass loss observed within 250÷350°C range on the TG curve corresponds to the loss of the ligand molecule per molecule of the compound (weight loss at 350°C, found 44.50%; calculated 45.20%). The process continues up to 492°C (residue: found 10.48%, calculated 12.02%).

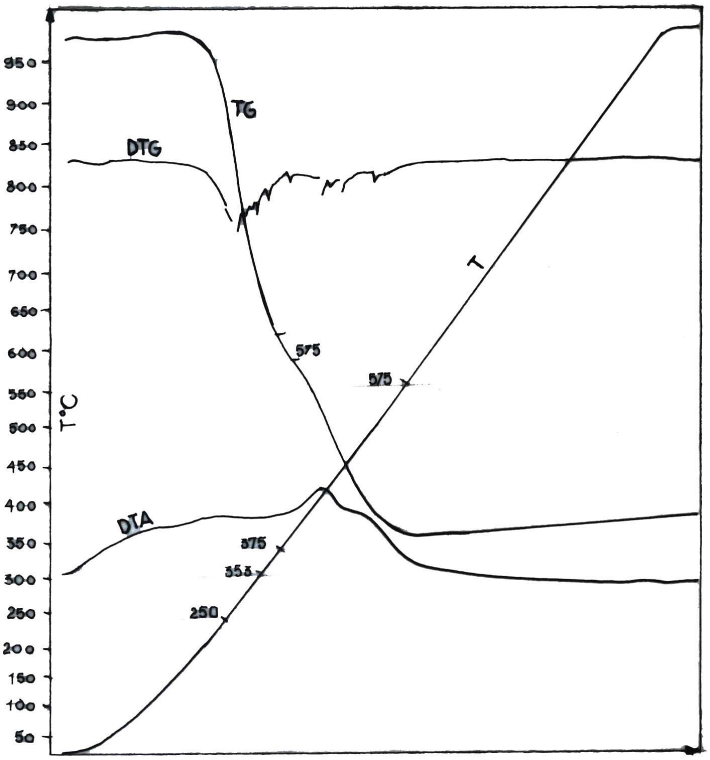


Fig. 2 *Thermodifferential curve of the compound 1'.*

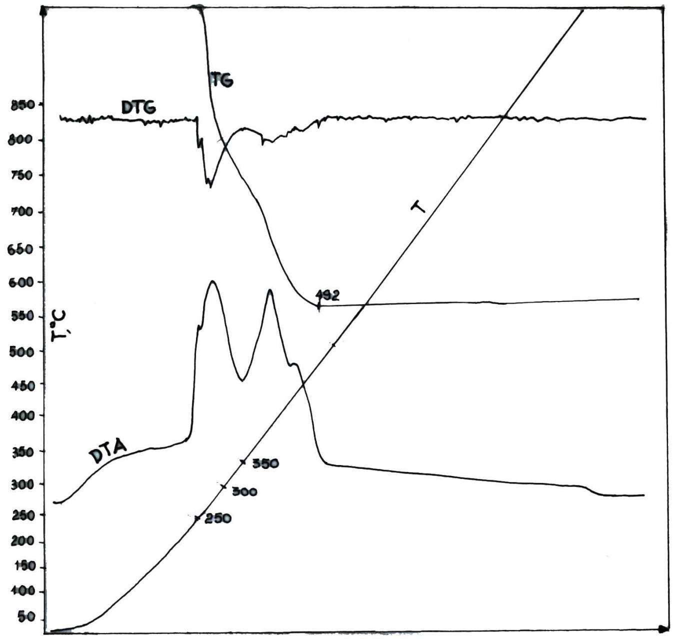


Fig. 3: *Thermodifferential curve of the compound 3.*

The IR spectra of the free ligands and of the complexes compounds recorded within 400÷4000 cm^{-1} range on KBr pellets offer information about the nature of the donor atoms (Table 4).

Table 4. The main absorption bands in the IR spectra (cm^{-1}) and their assignments

Ligand/ complex	ν_{OH}	ν_{NH}	$\nu_{C=O}$	$\nu_{C=N}$	$\nu(NO_2)_{asym}$	$\nu(NO_2)_{sym}$
B	-	3331w	1706m	1629s 1592vs	1507m	1337s
1	3464w	3331vw	1694w	1637vw 1590vs	1506s	1334s
1’	3464br	3333vw	1703w	1629m 1590vs	1507m	1335s
C	3600vw	3335m	1730vw	1680m 1620s 1570m	1502s	1333s
2	3540w	3480-3200br	1730vw	1660vw 1620w 1600s 1570m	1500s	1310m
D	3540-3300br,vs	-	1740vw	1650s 1610vs 1570vs	-	-
3	3440-3200m	-	1740w	1630m 1600m 1580w	-	-

vs – very strong. s – strong, m – medium, w – weak, vw – very weak, br - broad

The keto-enolic-enamine tautomerism (Scheme 1) is supported by the presence in IR spectra of free ligands of the bands due to ν_{OH}, ν_{NH}, $\nu_{C=O}$, $\nu_{C=N}$ and by the splitting of some bands supporting their NMR spectra. The nature, number and the position of the groups substituted on the benzene ring could explain the differences occurred in the shape intensity and position of this bands. The sharp band which occurs in 3140-3333 cm^{-1} range is rather due to ν_{NH} than ν_{OH} nonassociated (3600 cm^{-1}). The band $\nu_{C=O}$ (1706-1740 cm^{-1}) range characteristic for cyclic ketones appears as a sharp bands, medium, weak or very weak one and split in two peaks. The band due to $\nu_{C=N}$ (1629-1680 cm^{-1}) range appears a very strong or medium one with two or three peaks. The IR spectrum of ligand D presents a broad band 3300-3540 cm^{-1} with eight peaks unresolved could be assigned due to ν_{OH} associated suggesting intramolecular hydrogen bond as form (III) (Scheme 1).

The examination of the complex compounds spectra shows some remarks:

- For complex compounds noted 1 and 1' the sharp band (3331 cm^{-1}) appears as a very weak one, but it appears a new broad band centered at 3464 cm^{-1}. This new band could indicate the formation an intramolecular hydrogen bond as in form (II), Z or E (Scheme 1), upon the coordination to Cu(II) ion. The others bands ($\nu_{C=O}$ and $\nu_{C=N}$ show different changes. Thus, for the compound noted 1 the $\nu_{C=O}$ (1706 cm^{-1}) band is shifted to lower value 1694 cm^{-1} while the $\nu_{c=N}$ band (1629 cm^{-1}) is shifted to higher value 1637 cm^{-1}, but for the compound noted 1' their position are not changed, their intensity are modified, only. The bands due to $\nu(NO_2)_{asym}$ (1507 cm^{-1}) and $\nu(NO_2)_{sym}$ (1337 cm^{-1}) are not changed upon coordination. Thus, IR spectra of the compounds 1 and 1' could suggest that the ligand B acted monodentately by the N donor atom in tautomeric form (II), possible as both Z/E isomers.

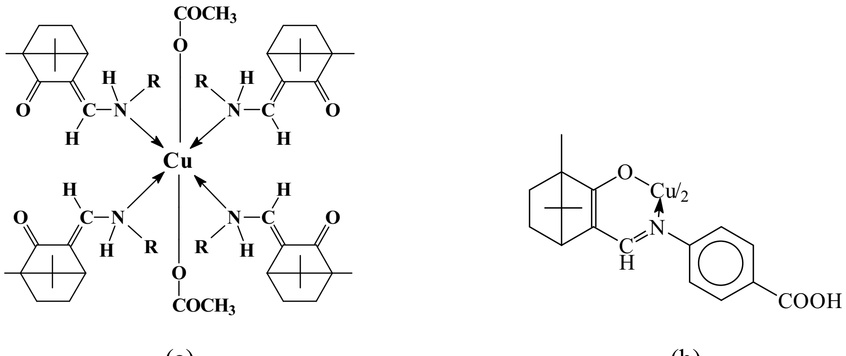
- In IR spectrum of the compound noted 2, the sharp band due to ν_{NH} (3335 cm^{-1} from IR spectrum of the free ligand appears as a broad band (3480-3200 cm^{-1}) and the band due to $\nu_{C=N}$ (1680 cm^{-1}) is shifted to lower value (1660 cm^{-1}). This could be as an argument for the coordination of the ligand C by N donor atom, the ligand C acting monodentately.

- The six-coordinated surrounding of the Cu(II) ion is due to axially bound acetate ion for the compounds noted 1, 1' and 2.

- For the compound CuD_2, noted 3, the band due to $\nu_{C=N}$ (1650 cm^{-1}) is shifted to lower value (1630 cm^{-1}) and very strong and broad band (3540-3300 cm^{-1} with eight peaks) from IR spectrum of free ligand appears as a medium one (3440-3100 cm^{-1}). These changes could suggest that ligand D act bidentately by both O and N donor atoms by the deprotonation of the OH group, making evident the participation of the ligand D in enolic tautomeric form.

- The assignments of the bands due to ν_{COO^-} (asymm) (1574 cm^{-1}) and ν_{COO^-} (symm) (1414 cm^{-1}) characteristic for acetate ion was not possible because of their overlapping with the bands present within range.

By correlating of the data of the chemical analysis, electronic, IR and EPR spectra, it was proposed following structural formula for compounds 1 (4.a) and 3 (4.b) (Fig. 4), where $R = p\text{-}NO_2\text{-}C_6H_5$.



(a) (b)

Fig. 4: *Structural formula proposed for the compounds 1 (a) and 3 (b).*

Conclusions

In the new complexes obtained, the Cu(II) ion is hexacoordinated (compounds 1, 1' and 2) and tetracoordinated in the compound 3.

The ligands B, C act monodentately by the N donor atom or O donor atom, but ligand D acts bidentately by both O and N donor atoms.

REFERENCES

1. Ciobanu, A., Zălaru, F., Baciu, I., Zălaru, Ch., Drăghici, C., Sferdean C. (2002) *Anal.Univ.Buc. (Serie nouă)* **XI**(1), 229-235
2. Percy, G.C. (1972) *J.Inorg.Nucl.Chem.* **34**, 3357.
3. Dudek, G.O., Holm, R.H. (1961) *J.Am.Chem.Soc.* **83**, 2029; Ibbid (1962) **84**, 2691.
4. Dudek, G.O. (1963) *J.Am.Chem.Soc.* **85**, 694-7.
5. Knorr, R., Ruf, F. (1985) *Chem.Ber.* **118**, 4486-95.
6. Hathaway, B.J., Billing, D.E. (1970) *Coord.Chem.Rev.* **5**, 143.
7. Hathaway, B.J. (1972) *J.Chem.Soc.(A)*, 1196.
8. Reedijk, J. (1970) *Rec.Trav.Chem.* **89**, 997.