

Metal Chelates of Heterocyclic Nitrogen-Containing Ketones. XIV. Metal Ion, Anion and Substituent Effects on the Enolization of Mono-Keto Compounds

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A number of new complexes of iron(II), cobalt(II), nickel(II), copper(II) and palladium(II) containing 2-picolyl-p-nitrophenyl- or 2-picolyl-p-tolyl ketone, L and L', respectively, and various anions (Cl^- , Br^- , NSC^- , BF_4^- or ClO_4^-) have been synthesized and characterized by elemental analyses, magnetic susceptibility, ESR, IR and reflectance spectral measurements. The stereochemistry and the nature of the complexes are markedly dependent upon the molar ratios of the reactants, the anions and the ligand substituents. In all complexes the ligands are chelated to the metal ion via the pyridine nitrogen and the carbonyl oxygen atoms, whereby in the case of $[ML_2]X_2$, $M = \text{iron(II)}$ and $[ML_3]X_2$, $M = \text{cobalt(II)}$ or nickel(II) and $X = ClO_4^-$ or BF_4^- , the 2-picolyl-p-nitrophenyl ketone exists in its enol form which is only deprotonated in the presence of palladium(II). The ligand field parameters (Dq , B' , λ and β) are calculated and related to the electronic environment and the basicity of the ligands.

Introduction

Heterocyclic nitrogen-containing ketones have attracted much attention, due to the biological implications of the heterocyclic base, and they form stereochemical interconvertible complexes [1–6]. As an extension of our studies on the mixed nitrogen–oxygen coordination and the substituent effects this work will report the ligation properties of 2-picolyl-p-nitrophenyl and 2-picolyl-p-tolyl ketones.

Experimental

Preparation of the Organic Ligands

The organic ligands were prepared according to the methods previously reported [4–6]. The compounds were established by the elemental analyses, Table I, and spectral properties. The melting points are 158 ± 1 and 138 ± 1 °C for L and L' respectively.

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Preparation and Analyses of Metal(II) Chelates

All halogeno- and perchlorate-complexes were prepared according to the following method, viz., an ethanolic solution of 0.01 mol of metal(II) salt (iron(II), cobalt(II), nickel(II), copper(II) or palladium(II) salts) was mixed with the appropriate weight of the corresponding ketone in ethanol (25–35 ml). The reaction mixture was boiled with stirring until the corresponding solid complex separated. On cooling the crystalline product formed in each case was filtered off, washed several times with ethanol, and dried under vacuum over P_2O_5 .

The thiocyanato-complexes were prepared as follows: ethanolic solutions of $M(NO_3)_2 \cdot 6H_2O$, $M = \text{cobalt(II)}$ or nickel(II) , and equivalent amounts of solid KSCN or NH_4SCN were mixed and refluxed for 30 min. After cooling in an ice-bath, the precipitate KNO_3 was filtered off and the filtrate was concentrated by slow evaporation on a steam bath. On addition of the appropriate quantity of the corresponding ketone in ethanol (30 ml), a microcrystalline solid was deposited. The resulting solid compound was cooled and filtered on a porous glass filter, washed several times with ethanol, and dried under vacuum over P_2O_5 .

The tetrafluoroborate-complexes were prepared in the following way; hexa-aquo metal(II) bistetrafluoroborate (0.01 mol) was dissolved in excess of triethylorthoformate (0.1 mol). After 2 hr, the solvent was evaporated under reduced pressure. The residue was taken up in $MeNO_2$ (30 ml). This solution was added to 0.035 mol of the corresponding ketone in $MeNO_2$ (30 ml). After stirring for 2–3 hr at room temperature, the crystalline solid was filtered off, washed several times with ethanol followed by diethyl ether, and dried under vacuum over P_2O_5 .

Carbon, nitrogen, hydrogen, halogen and sulphur contents were done at the Microanalytical Laboratory of Cairo University. The metal(II) content in each complex was determined according to the methods previously reported [5, 7]. The elemental analyses are given in Table I.

TABLE I. Analytical and Molar Conductivity* Data.

Compound	Λ_M^* % Found (Calculated)					
	C	H	N	M	X	
L	—	64.3(64.5)	4.0(4.1)	11.5(11.6)	—	—
L'	—	79.5(79.6)	6.1(6.2)	6.5(6.6)	—	—
1 [CuLCl ₂]	3.8	41.3(41.4)	2.6(2.6)	7.3(7.4)	16.9(16.9)	18.8(18.9)
2 [CuLBr ₂]	4.2	33.5(33.5)	2.1(2.2)	6.0(6.0)	13.6(13.7)	17.1(17.2)
3 [CuL ₂]Cl ₂	255.0	50.2(50.4)	3.1(3.2)	9.0(9.1)	10.2(10.3)	11.4(11.5)
4 [CuL ₂]Br ₂	261.2	44.0(44.1)	2.8(2.8)	8.0(7.9)	8.9(9.0)	22.5(22.6)
5 [CuL'Cl ₂]	3.4	48.7(48.6)	3.9(3.8)	4.1(4.1)	18.3(18.2)	20.0(20.0)
6 [CuL'Br ₂]	4.1	38.7(38.7)	3.0(3.0)	3.3(3.2)	14.6(14.6)	36.9(36.8)
7 [CuL ₂ ']Cl ₂	249.6	60.3(60.4)	4.6(4.7)	5.1(5.0)	6.5(6.6)	12.7(12.8)
8 [CuL ₂ ']Br ₂	258.9	52.0(52.1)	4.1(4.0)	4.4(4.3)	9.9(10.0)	24.7(24.8)
9 [CoLCl ₂]	3.9	41.7(41.9)	2.7(2.7)	7.6(7.5)	15.7(15.8)	19.0(19.1)
10 [CoLBr ₂]	3.1	33.6(33.8)	2.1(2.2)	6.0(6.1)	12.7(12.7)	34.6(34.7)
11 [CoL(NCS) ₂]	4.1	42.9(43.0)	2.3(2.3)	13.5(13.4)	14.1(14.1)	15.2(15.4)•
12 [CoL ₂]Cl ₂	250.1	50.6(50.8)	3.2(3.3)	9.1(9.1)	9.6(9.6)	11.4(11.6)
13 [CoL ₂]Br ₂	261.3	44.3(44.4)	2.9(2.9)	7.8(7.9)	8.4(8.4)	22.6(22.7)
14 [CoL ₃](ClO ₄) ₂	164.6	47.6(47.6)	3.1(3.0)	8.4(8.5)	6.0(6.0)	7.4(7.3)
15 [CoL ₃](BF ₄) ₂	138.8	48.6(48.8)	3.0(3.1)	8.8(8.7)	6.1(6.1)	—
16 [CoLCl ₂]	4.8	49.1(49.3)	3.7(3.8)	4.0(4.1)	17.2(17.3)	20.6(20.8)
17 [CoL'Br ₂]	4.2	38.9(39.1)	3.0(3.0)	3.1(3.0)	13.7(13.7)	37.0(37.2)
18 [CoL'(NCS) ₂]	5.3	49.6(49.7)	3.3(3.4)	10.8(10.9)	15.2(15.3)	16.5(16.6)•
19 [CoL ₂ ']Cl ₂	265.0	60.6(60.8)	4.6(4.7)	5.0(5.1)	10.7(10.7)	12.8(12.9)
20 [CoL ₂ ']Br ₂	250.9	52.5(52.4)	4.0(4.1)	4.3(4.4)	9.3(9.2)	25.0(25.0)
21 [CoL ₃ '](ClO ₄) ₂	162.7	56.3(56.2)	4.3(4.4)	4.7(4.7)	6.6(6.6)	8.0(7.9)
22 [CoL ₃ '](BF ₄) ₂	135.5	58.0(58.2)	4.5(4.5)	4.8(4.9)	6.7(6.8)	—
23 [NiLCl ₂]	6.1	41.8(41.9)	2.6(2.6)	7.5(7.5)	15.9(15.8)	19.0(19.1)
24 [NiLBr ₂]	5.7	33.8(33.9)	2.2(2.2)	6.0(6.1)	12.7(12.7)	34.8(34.7)
25 [NiL(NCS) ₂]	4.8	43.3(34.2)	2.3(2.4)	13.3(13.4)	14.1(14.1)	15.2(15.3)•
26 [NiL ₂]Cl ₂	4.4	50.9(50.8)	3.2(3.3)	9.0(9.1)	9.5(9.6)	11.5(11.6)
27 [NiL ₂]Br ₂	4.7	44.2(44.4)	2.8(2.8)	8.0(7.9)	8.3(8.4)	22.7(22.8)
28 [NiL ₂ (NCS) ₂]	3.9	51.0(51.0)	2.9(3.0)	12.7(12.7)	8.9(8.9)	9.6(9.7)•
29 [NiL ₃](ClO ₄) ₂	158.3	47.4(47.6)	3.0(3.0)	8.4(8.5)	5.9(5.9)	7.1(7.2)
30 [NiL ₃](BF ₄) ₂	138.1	48.7(48.8)	3.0(3.1)	8.7(8.7)	6.0(6.1)	—
31 [NiL'Cl ₂]	3.9	49.2(49.3)	3.8(3.8)	4.0(4.1)	17.2(17.2)	20.7(20.8)
32 [NiL'Br ₂]	6.2	39.0(39.1)	3.0(3.0)	3.2(3.3)	13.6(13.7)	37.0(37.2)
33 [NiL'(NCS) ₂]	5.8	49.6(49.8)	3.3(3.2)	10.7(10.8)	15.2(15.2)	16.5(16.6)•
34 [NiL ₂ ']Cl ₂	4.4	60.8(60.9)	4.7(4.7)	5.0(5.1)	10.6(10.6)	12.7(12.8)
35 [NiL ₂ ']Br ₂	5.3	52.2(52.4)	4.0(4.1)	4.3(4.3)	9.1(9.2)	25.0(24.9)
36 [NiL ₂ '](NCS) ₂	5.4	60.2(60.3)	4.4(4.4)	9.2(9.3)	9.8(9.8)	10.5(10.6)•
37 [NiL ₃ '](ClO ₄) ₂	168.3	56.3(56.4)	4.3(4.4)	4.7(4.7)	6.5(6.6)	88.0(7.9)
38 [NiL ₃ '](BF ₄) ₂	133.3	58.1(58.2)	4.5(4.5)	4.7(4.8)	6.8(6.8)	—
39 [PdLCl ₂]	3.6	40.5(40.7)	2.3(2.3)	7.4(7.3)	27.7(27.8)	9.1(9.3)
40 [PdLBr ₂]	4.7	36.4(36.5)	2.1(2.1)	6.5(6.5)	24.9(25.0)	18.6(18.7)
41 [PdL ₂]Cl ₂	4.3	47.0(47.2)	3.1(3.0)	8.3(8.5)	16.0(16.1)	10.6(10.7)
42 [PdL ₂]Br ₂	4.2	41.7(41.6)	2.6(2.7)	7.4(7.5)	14.0(14.2)	21.1(21.3)
43 [PdL ₂]·3H ₂ O	1.3	48.4(48.4)	2.8(2.8)	8.5(8.7)	16.5(16.6)	8.3(8.4)''
44 [FeL ₂](BF ₄) ₂	137.8	43.3(43.4)	2.8(2.8)	7.7(7.8)	7.8(7.8)	—
45 [FeL ₂](ClO ₄) ₂	166.4	42.1(42.2)	2.8(2.7)	7.5(7.6)	7.5(7.6)	9.5(9.7)
46 [PdL'Cl ₂]	3.9	43.2(43.2)	3.2(3.3)	3.6(3.6)	27.2(27.3)	18.4(18.3)
47 [PdL'Br ₂]	4.8	32.5(32.7)	2.7(2.7)	2.8(2.9)	22.1(22.3)	33.3(33.5)
48 [PdL ₂ ']Cl ₂	3.7	56.0(56.1)	4.2(4.3)	4.6(4.7)	17.7(17.8)	11.6(11.8)
49 [PdL ₂ ']Br ₂	3.9	48.8(48.8)	3.7(3.8)	4.0(4.1)	15.4(15.4)	23.0(23.2)

*Molar conductivity as $10^{-3} M$ in MeNO₂ ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$). •% of sulphur. ''% of water in molecule.

L = 2-picoyl-p-nitrophenyl ketone and L' = 2-picoyl-p-tolyl ketone.

Physical Measurements

The diffuse reflectance spectra were recorded with a CARY 14 spectrophotometer. IR spectra were obtained as KBr discs with a UNICAM SP 2000 spectrophotometer. ESR data were obtained with a VARIAN spectrometer at X-band and DPPH was used as a reference. Magnetic measurements were carried out at room temperature using the Gouy method and the diamagnetic corrections were calculated by the use of Pascal's constants [8]. The molar conductance of the complexes as 10⁻³ M solution in MeNO₂ was measured at 25 °C with a SIEMENS conductivity bridge using platinum electrodes, and is given in Table I.

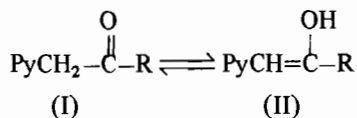
Results and Discussion

General

The complexes are listed in Table I with their elemental analyses and conductivity data. They are stable in air and sparingly soluble in chloroform, nitrobenzene, dichloromethane and nitromethane, and insoluble in ethanol and acetone. From the stoichiometries of all complexes it is clear that the ligands function as bidentate oxygen-nitrogen donors.

The Infrared Spectra

The infrared spectra of some heterocyclic nitrogen containing ketones have been studied and the assignments of their IR bands were reported [4-7]. By analogy with these assignments, the IR spectral bands of 2-picoly-p-nitrophenyl ketone, L, and 2-picoly-p-tolyl ketone, L', with tentative assignments have been set up and given in Tables II and III. The free ketones have the following structures with predominant formula I [4, 5]:



The IR spectra of both ketones are similar and exhibit bands at 3130-3150, 1605-1620 and 635-640 cm⁻¹ due to $\nu\text{C-H}$, $\nu\text{C=N}$ and δPy , respectively. The ring breathing in the two ligands are traced at 980-990 cm⁻¹. The bands at 1410-1415 cm⁻¹ are assigned to $\delta\text{C-H}$ whereas those at 1210-1215 cm⁻¹ are due to $\nu\text{C-C}$. The main difference between the IR spectral bands is due to the $\nu\text{C=O}$, where it appears at 1740 and 1650 cm⁻¹ for L and L', respectively. The higher position of the carbonyl stretching frequency of 2-picoly-p-nitro-phenyl ketone could be attributed to the increased force

TABLE II. Infrared Absorption Bands (cm⁻¹) of 2-Picoly-p-nitrophenyl Ketone and Its Metal(II) Chelates.

Compd.*	$\nu\text{C=O}$	$\nu\text{C=N}$	$\nu\text{C-H}$	Ring breathing	νOH	$\nu\text{C=C}$	$\nu\text{M-O}$	$\nu\text{M-N}$	$\nu\text{M-X}$
L	1740vs	1620s	3140m	900m	-	-	-	-	-
1	1712vs	1598m	3150m-w	1006m	-	-	528m	306m	272s
2	1708s	1586m	3150w	1010m	-	-	520m	298m	226s
3	1710m-s	1580m	3155m	1018w	-	-	525m	305m	-
4	1710s	1582s	3152m	1016m	-	-	528m	305m	-
9	1698s	1585s	3150m	1020w	-	-	392m	470m	342s
10	1690s	1590s	3150m-w	1018m	-	-	395m	476m	254s
11	1700s	1580s	3150m	1020m	-	-	398m	474m	280w
12	1696s	1588m-s	3152m	1022w	-	-	395m	476m	-
13	1698s	1584s	3150m	1020w	-	-	398m	480m	-
14	-	1590s	3156w	1026w	3390br	1478m	400m	476m	-
15	-	1586s	3158m	1024m	3396br	1475m	400m	476m	-
23	1705m-s	1590s	3152m	1005w	-	-	330m	435m	255s
24	1700s	1588s	3150m	1010m	-	-	332m	442m	220s
25	1710s	1596s	3155w	1008m	-	-	334m	438m	278w
26	1708s	1582s	3145m	1006w	-	-	332m	442m	262s
27	1698s	1585s	3158m	1008m	-	-	336m	440m	218m
28	1710s	1580m	3150m	1008w	-	-	332m	448m	280w
29	-	1585s	3152m	1020w	3400br	1476m	336m	438m	-
30	-	1590m	3150m	1022w	3402br	1480m-s	336m	440m	-
39	1712vs	1585s	3150m	1005m	-	-	295m	480m	280s
40	1712s	1582m	3150m	1002w	-	-	290m	490m	218s
41	1718s	1586m	3150m	1000m	-	-	-	480m	335s
42	1715s	1582m	3150m	1002m	-	-	-	472m	262s
43	-	1586s	3150m	1000m	3220br ^a	1480m	296m	485m	-
					3400				

*Compound numbers are as listed in Table I. ^aIR absorption due to the free H₂O. vs = very strong, m = medium, w = weak, br = broad.

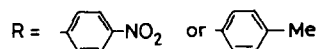
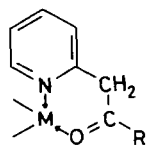
TABLE III. Infrared Absorption Bands (cm^{-1}) of 2-Picolyl-p-tolyl Ketone and Its Metal(II) Chelates.

Compd.*	$\nu\text{C}=\text{O}$	$\nu\text{C}=\text{N}$	$\nu\text{C}-\text{H}$	Ring breathing	$\nu\text{M}-\text{O}$	$\nu\text{M}-\text{N}$	$\nu\text{M}-\text{X}$
L'	1650vs	1605vs	3135m	980m	—	—	—
5	1618s	1566m-s	3146m	1000m	500m	312s	268s
6	1626s	1565m	3145m	1005m-w	496m	305s	220s
7	1630m-s	1565m	3145m	1008w	492m	305m-s	—
8	1630m	1568m-w	3150m	1010m	494m-s	308s	—
16	1620s	1560s	3150m	1005m	386m	472s	344s
17	1625m	1562m	3148m	1010m	390s	470s	262s
18	1622s	1564m-s	3145m	1000w	385m	465s	278w
19	1620s	1555m	3148m	1005w	392s	470s	—
20	1625s	1560s	3148m	1010m	395m	475s	—
21	1628m-s	1565m	3155m	1015m-w	390m-s	470s	—
22	1630s	1560s	3155m	1015w	385m	476s	—
31	1634s	1565m	3150m	1010w	366m	445s	260s
32	1635m-s	1560m	3150m-w	1012w	358m	450s	220m
33	1635s	1565m	3150w	1015w	365m	455s	266w
34	1630s	1560m-s	3150w	1010m	360m	460s	270s
35	1635m-s	1568m	3152w	1008m	364m-s	468s	225m
36	1638s	1565m-s	3155m	1010m-w	365m	465s	272w
37	1635m-s	1570m	3150m	1015w	360m	455m	—
38	1630s	1568m	3150m	1015w	365m	460m	—
46	1635m-s	1575m	3145m	1005w	295m	480m-s	340s
47	1630s	1570s	3146m	1008m	292m	485s	275s
48	1626s	1565m	3145m	1000m	—	475w-m	335s
49	1630s	1565m	3145m	1000w	—	480m	265s

*Compound numbers are as listed in Table I. vs = very strong, s = strong, m = medium and w = weak.

constant as a result of the electron withdrawing character of p-nitrophenyl group attached to the carbonyl carbon.

The IR spectra of all metal(II) complexes (except $[\text{ML}_3]\text{X}_2$, M = cobalt(II) or nickel(II), X = ClO_4^- or BF_4^- and $\text{PdL}_2 \cdot 3\text{H}_2\text{O}$) are similar, Tables II and III. In all complexes the ring breathing exhibits upward shift by ca. $15\text{--}25\text{ cm}^{-1}$ but the bands due to $\nu\text{C}=\text{O}$ and $\nu\text{C}=\text{N}$ exhibit downward shift by ca. $25\text{--}30$ and $35\text{--}40\text{ cm}^{-1}$, respectively. Also the band due to δPy is shifted to higher frequencies (ca. $10\text{--}15\text{ cm}^{-1}$) with splitting. According to these IR data and the observations in our previous work [4–7], the ligands act as neutral bidentate chelating agents as shown below:

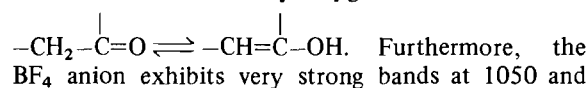


M = iron(II), cobalt(II), nickel(II), copper(II), or palladium(II)

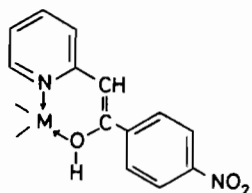
The thiocyanato-complexes exhibit IR absorptions at $2025\text{--}2040$ (νNCS), $860\text{--}875$ ($\nu\text{C}-\text{S}$) and a medium band at $480\text{--}490\text{ cm}^{-1}$ (δNCS), which are characteristic of the monodentate N-bonded thiocyanate [8]. This is confirmed by the appearance of strong to medium absorption at $260\text{--}280\text{ cm}^{-1}$, Tables II and III, characteristic of $\nu\text{M}-\text{NCS}$.

The non-electrolyte halogeno-complexes (except $[\text{PdLX}]_2$, X = Cl^- or Br^-) exhibit far IR absorptions, indicating a terminal coordinated halide ion [9]. Also, the $\nu\text{M}-\text{N}_{\text{lig}}$ are traced in the far IR region and are given in Tables II and III.

The IR spectra of tetrafluoroborate- and perchlorate-complexes, $[\text{ML}_3]\text{X}_2$, M = cobalt(II) or nickel(II) and X = ClO_4^- or BF_4^- , are strongly different from the rest of complexes, Table II. The most striking differences are the disappearance of the strong band at 1740 cm^{-1} ($\nu\text{C}=\text{O}$) and the appearance of a moderate one at $3390\text{--}3400\text{ cm}^{-1}$ which could be assigned to νOH . Also, the band at 1215 cm^{-1} ($\nu\text{C}-\text{C}$) has disappeared and additional bands at $1470\text{--}1480\text{ cm}^{-1}$ and $865\text{--}875\text{ cm}^{-1}$ are observed and assigned to $\nu\text{C}-\text{O}$ and $\nu\text{C}-\text{N}$ respectively [9]. This means that one of the methylene protons was transferred to the carbonyl oxygen as:



530 cm^{-1} but not those at 750 and 350 cm^{-1} , indicating a tetrahedral symmetry of the tetrafluoroborate anion [7]. The perchlorate anion exhibits bands at 1180–1200, 830–840 and 620–625 cm^{-1} due to the non-coordinated ClO_4^- [9, 10]. Accordingly, the following formula could be assumed for these chelates.



M = cobalt(II), nickel(II), or iron(II)

Magnetic and Spectral Studies

Copper(II) complexes

The interaction of copper(II) salts with L and L' yielded complexes of stoichiometries, $[\text{CuLX}_2]$, $[\text{CuL}'\text{X}_2]$, $[\text{CuL}_2]\text{X}_2$ and $[\text{CuL}'_2]\text{X}_2$, X = Cl^- or Br^- . The 1:1 complexes are non-electrolytes while the 1:2 complexes have molar conductivity values consistent with 1:2 electrolyte types in 10^{-3} M solution in MeNO_2 , Table I.

The effective magnetic moments measured at room temperature, Table IV, indicate that the copper(II) complexes are magnetically dilute [11, 12]. The solid reflectance and MeNO_2 solution spectra of $[\text{MLX}_2]$ and $[\text{ML}'\text{X}_2]$ complexes are given in Table IV. The spectra showed a broad band with a shoulder in the 17040–10300 cm^{-1} range.

TABLE IV. Magnetic, Electronic and ESR Spectral Data of Copper(II) Complexes.

Compd. ^a	$\mu_{\text{eff.}}^{\text{b}}$ (B.M.)	Electronic spectra		Electron spin resonance data					
		Solid	MeNO_2 (log ϵ)	ϵ_1 ϵ_{\parallel}	ϵ_2	ϵ_3 ϵ_{\perp}	$\epsilon_{\text{av.}}$	G	A_{11}^{c}
1	1.77	17430 10760	17305(2.12) 10720sh	2.290		2.060	2.140	4.39	—
2	1.76	17060 10420	17100(2.02) 10370sh	2.250		2.060	2.120	4.17	—
3	2.04	18600 14500 13700 11400 7100	17830(2.45) 15630(2.31) 13730(2.20) 12500(2.03) 7090(1.09)	2.048	2.120	2.310	2.159	—	61
4	2.02	18380 14500 13660 12080	18090(2.51) 15640(2.02) 13710(2.00) 11980(1.92) 7100(1.02)	2.053	2.118	2.308	2.160	—	60
5	1.78	17280 10833	17300(2.07) 10800sh	2.230		2.040	2.100	5.75	—
6	1.75	17090 10900	17020(2.14) 10820sh	2.210		2.050	2.100	4.20	—
7	2.03	18520 14280 13890 12300	18075(2.63) 15630(2.30) 13900(2.11) 12180(2.01) 7000(1.04)	2.041	2.089	2.360	2.163	—	60
8	2.13	18490 14280 13890 11980	18460(2.76) 14300(2.20) 13900(2.09) 12000(2.00) 7110(1.19)	2.039	2.091	2.370	2.166	—	62

^aCompound numbers are as listed in Table I. ^bMeasured at room temperature. ^c $A_{11} \times 10^4 \text{ cm}^{-1}$. sh = shoulder.

These spectra are similar to those reported for square planar copper(II) complexes [12, 13]. The solid reflectance and MeNO_2 solution spectra of $[\text{CuL}_2]\text{X}_2$ and $[\text{CuL}'_2]\text{X}_2$ are given in Table IV. The spectra are consistent with the data reported for bis-(*t*-butyl salicylidaminato)copper(II) which has a distorted tetrahedral symmetry [4, 14].

The X-band ESR spectra of the polycrystalline samples of the mono(ligand)copper(II) complexes, Table IV, are typical of those reported for axial type copper(II) complexes and are consistent with a primarily $d_{x^2-y^2}$ ground state for a species having elongated tetragonal or square planar structure [14, 15]. Typical spectra are shown in Fig. 1 and the results are given in Table IV. In an axial symmetry ($g_{\parallel} > g_{\perp}$), the g -values are related by the expression $G = g_{\parallel} - 2/g_{\perp} - 2$, which measures the exchange interaction between copper centers in the polycrystalline solid [14, 15]. The calculated G -values are larger than four, indicating that the exchange interaction could be neglected [15]. The average g -values were calculated according to the relation, $g_{\text{av.}} = 1/3g_{\parallel} + 2/3g_{\perp}$, Table IV. The calculated $g_{\text{av.}}$ are in agreement with an orbitally non-degenerate state [14, 15].

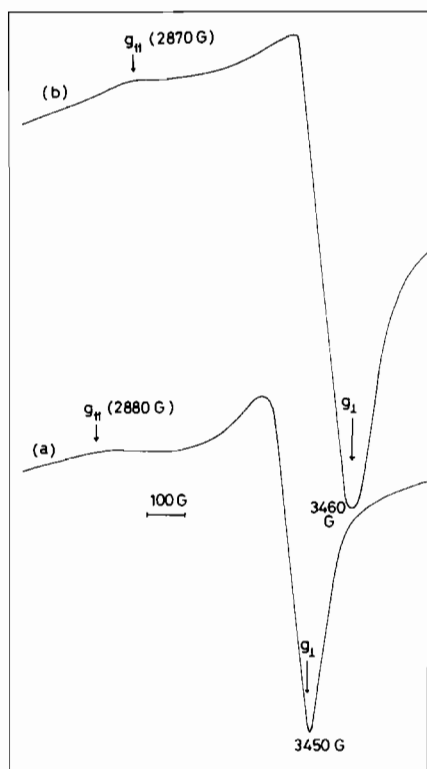


Fig. 1. X-band ESR spectra of polycrystalline (a) $[\text{CuLCl}_2]$, (b) $[\text{CuL}'\text{Cl}_2]$, at 25 °C.

The X-band ESR spectra of $[\text{CuL}_2]\text{X}_2$ and $[\text{CuL}'_2]\text{X}_2$, $\text{X} = \text{Cl}^-$ or Br^- , as polycrystalline samples at 25 °C are shown in Fig. 2. The spectra are characteristic

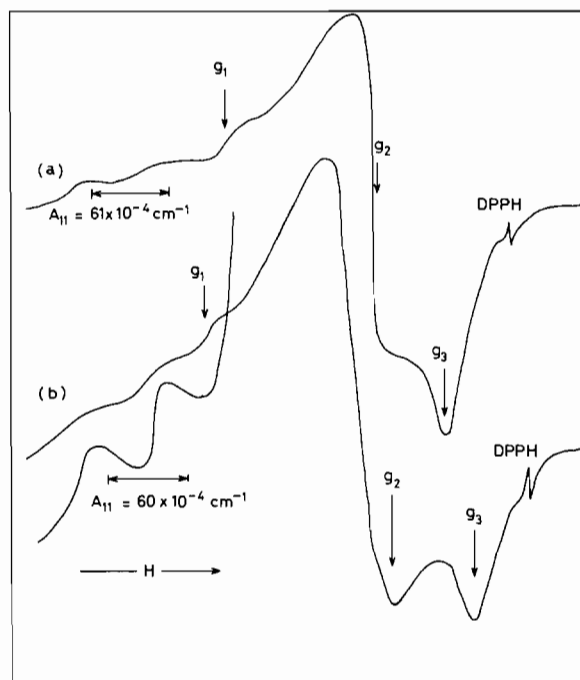


Fig. 2. X-band ESR spectra of polycrystalline (a) $[\text{CuL}_2]\text{Cl}_2$, (b) $[\text{CuL}'_2]\text{Cl}_2$, at room temperature.

of rhombic symmetry and gave three distinct g -values with $g_3 > g_2 > g_1$. The super-exchange splitting constant A_{11} was obtained from the spectrum of each complex and is given in Table IV. The small A_{11} values and the shape of the spectra exhibit similarities with comparable data for the blue copper proteins [17], characterized by small values of the parallel electron spin–nuclear spin hyperfine coupling constants ($A_{11} \leq 100 \times 10^{-4} \text{ cm}^{-1}$). An inspection of the published ESR spectra of the blue proteins shows that the isotropic hyperfine coupling constants lie in the range $20\text{--}40 \times 10^{-4} \text{ cm}^{-1}$. This means that if the blue copper proteins could tumble rapidly in solution, only single-line ESR spectra could be obtained. The origin of the small hyperfine coupling constants in the pseudotetrahedral copper(II) complexes is associated with metal 4s and 4p orbital admixture into the ground state [18].

Cobalt(II) complexes

The room temperature magnetic moments of $[\text{CoLX}_2]$, $[\text{CoL}'\text{X}_2]$, $[\text{CoL}_2]\text{X}_2$ and $[\text{CoL}'_2]\text{X}_2$, $\text{X} = \text{Cl}^-$, Br^- , or NCS^- , are given in Table V. The moments are normal for tetrahedral cobalt(II) complexes [4]. The molar conductivity of these complexes as 10^{-3} M in MeNO_2 given in Table I shows that $[\text{CoLX}_2]$ and $[\text{CoL}'\text{X}_2]$ are non-electrolytes while $[\text{CoL}_2]\text{X}_2$ and $[\text{CoL}'_2]\text{X}_2$ are 1:2 electrolytes.

The solid reflectance and MeNO_2 solution spectra of these complexes exhibit bands with shapes and positions characteristic of tetrahedral cobalt(II)

TABLE V. Magnetic Data (B.M.) and Ligand Field Parameters (cm^{-1}) of Cobalt(II) Complexes.

Compd.*	μ_{eff}	ν_1	ν_2	ν_3	10Dq	B'	β	$-\lambda$	Dq/B'
9	4.47		5580	14660	3236	702	0.73	120	—
10	4.44		5260	14380	3054	633	0.65	108	—
11	4.50	—	5835	14995	3384	712	0.74	132	—
12	4.47	—	6580	15980	3816	740	0.76	142	—
13	4.46	—	6590	16010	3822	742	0.77	140	—
14	5.12	8380	—	20130	9553	888	0.92	—	1.08
15	5.20	8335	—	20050	9502	884	0.91	—	1.07
16	4.53	—	6060	14790	3515	687	0.71	144	—
17	4.51	—	5765	14495	3344	682	0.70	133	—
18	4.54	—	6140	15070	3561	702	0.73	148	—
19	4.46	—	6740	16030	3909	736	0.76	142	—
20	4.46	—	6745	16040	3912	736	0.76	143	—
21	5.03	8670	—	20978	9884	919	0.95	—	1.08
22	4.98	8560	—	21320	9758	908	0.94	—	1.07

*Compound numbers are as in Table I.

complexes [9]. The ν_3 and ν_2 transitions necessary to evaluate the spectrochemical parameters by means of the Tanabe–Sugano equation were estimated visually [20, 21]. The chosen ν_2 and ν_3 together with the calculated spectral parameters are given in Table V. The Dq-values for this series of cobalt(II) complexes are found to be higher in the case of the 2-picoyl-p-nitrophenyl ketone than those containing 2-picoyl-p-tolyl ketone. This is due to the higher basicity of the latter ligand. Also, the complexes $[\text{CoL}'\text{X}_2]$ and $[\text{CoL}'_2\text{X}_2]$ have higher B' values than $[\text{CoLX}_2]$ and $[\text{CoL}_2\text{X}_2]$, respectively, indicative of a considerable orbital overlap and delocalization of the d-orbitals of cobalt(II) ion *i.e.* higher covalent character of the p-nitrophenyl-complexes than the other.

The application of the rule of the average environment [22] showed that the spectral parameters are in agreement with the mixed nitrogen–oxygen donation [23]. The spin–orbit coupling constant (λ) calculated by the equation [21], $\mu_{\text{obs.}} = \mu_{\text{s.o.}} - 15.59\lambda/10\text{Dq}$, was found to be in the range 132–108 and 144–133 cm^{-1} for L and L', respectively. The lower values of the spin–orbit coupling constant of all complexes than that of the free ion (178 cm^{-1}) gave a reduction of 17–39%, indicating a spin–orbit coupling effect. Furthermore, the lowering of the spin–orbit coupling constant is found to be in the sequence $\text{NCS}^- > \text{Cl}^- > \text{Br}^-$, especially in $[\text{CoLX}_2]$ and $[\text{CoL}'\text{X}_2]$, X = Cl^- , Br^- or NCS^- .

The complexes of stoichiometry, $[\text{CoL}_3\text{X}_2]$ and $[\text{CoL}'_3\text{X}_2]$, X = ClO_4^- or BF_4^- are 1:2 electrolytes in MeNO_2 (10^{-3} M solution), Table I. The room temperature effective magnetic moments of these complexes lie in the 5.20–4.98 B.M. range, Table V, characteristic of octahedral cobalt(II) complexes [4]. Their electronic spectra either as solid reflectance or as CHCl_3 solution exhibit bands typical for

octahedral symmetry. The ligand field spectra and the calculated spectral parameters are given in Table V, and are consistent with the expected nitrogen–oxygen donation [23].

Nickel(II) complexes

The interaction of nickel(II) salts with L or L' afforded complexes of stoichiometries, $[\text{NiLX}_2]$, $[\text{NiL}'\text{X}_2]$, $[\text{NiL}_2\text{X}_2]$ and $[\text{NiL}'_2\text{X}_2]$, X = Cl^- , Br^- or NCS^- . Also complexes of stoichiometry, $[\text{NiL}_3\text{X}_2]$ and $[\text{NiL}'_3\text{X}_2]$, X = ClO_4^- or BF_4^- , were isolated and characterized. The mono(ligand)nickel(II) complexes are non-electrolytes in MeNO_2 (10^{-3} M solution). Their ligand field spectra did not show any absorption in the near IR region. This suggests that the ground state of nickel(II) ion in the $[\text{NiLX}_2]$ and $[\text{NiL}'\text{X}_2]$ complexes is the ${}^1\text{A}_{1g}$, in accordance with their diamagnetism. The ligand field spectra of these chelates were found to be dependent upon the nature of the anion in the sequence $\text{NCS}^- > \text{Cl}^- > \text{Br}^-$. Based on these spectral studies, the nature of the ligands and the IR data, square planar geometry could be assumed for these chelates, Table VI.

The room temperature magnetic moments of the bis- and tris(ligand) nickel(II) complexes lie in the 3.28–3.08 B.M. range, Table VII, and are consistent with the paramagnetic six-coordinate nickel(II). The molar conductivity of $[\text{NiL}_2\text{X}_2]$ and $[\text{NiL}'_2\text{X}_2]$ indicates their non-electrolytic nature, while for $[\text{NiL}_3\text{X}_2]$ and $[\text{NiL}'_3\text{X}_2]$ it indicates that they are 1:2 electrolytes.

The solid reflectance and CHCl_3 solution spectra of the bis(ligand)nickel(II) complexes exhibit bands typical for nickel(II) in octahedral environment. The spectra showed three well-defined transitions between the triplet states in this geometry, with some evidence of tetragonal distortion, Table VII. As the symmetry is lowered to D_{4h} (since the in-plane

TABLE VI. Solid Reflectance and Solution Spectra, cm^{-1} ($\log \epsilon$) of Mono(ligand)nickel(II) Complexes.

Compd.	Med.	C.T.	ν_3	ν_2	ν_1
23	solid	28350,25270	20350	17350sh	15330sh
	MeNO ₂	28630(4.1),24940(3.4)	19975(3.3)	18040(1.22)	15380(1.03)
24	solid	29390,23750	19740	17680sh	15000sh
	MeNO ₂	29005(4.2),23130(2.9)	19890(3.1)	17480(1.34)	15.105(1.03)
25	solid	29940,24800	21240	17830sh	15980sh
	MeNO ₂	29890(4.4), 25000(3.8)	21450(3.2)	18230(1.27)	16020(1.01)
31	solid	26350,23700	18780	16380sh	14790sh
	MeNO ₂	26850(4.9),24000(3.6)	18460(3.3)	16880(1.29)	14870(1.06)
32	solid	27050,24200	18490	16420sh	14250sh
	MeNO ₂	27580(4.9),23920(3.6)	18530(3.1)	16600(1.41)	14315(1.01)
33	solid	26900,24300	18990	16800sh	15210sh
	MeNO ₂	27000(5.1),24410(4.7)	18830(3.7)	16930(1.32)	15420(1.05)

TABLE VII. Magnetic Data (B.M.) and Ligand Field Parameters (cm^{-1}) of Bis(ligand)nickel(II) Complexes.

Compd.*	Electronic spectra	Dq ^{xy}	Dq ^z	Dt	DT	DQ	DQ ^L	DQ ^Z	DT/DQ	μ_{eff}
26	10480,11680,16420,28520	1168	928	137	1858	29915	32114	25519	0.06	3.30
27	10500,11800,16950,28480	1180	920	148	2013	30063	32445	25299	0.07	3.21
28	9840,11420,16450,28350	1142	826	188	2555	28377	31401	22330	0.09	3.15
34	10500,11820,16450,28250	1182	918	151	2047	30077	32499	25232	0.07	3.28
35	10250,11950,16720,27700	1195	855	194	2630	29745	32857	23520	0.09	3.14
36	9500,11400,16950,27850	1140	760	218	2955	27850	31347	20856	0.11	3.12

ligands consist of two oxygen and two nitrogen atoms, the symmetry is strictly D_{2h}, the ³A_{2g} → ³T_{2g} transition in this octahedral symmetry is split into ³B_{1g} → ³B_{2g} and ³B_{1g} → ³E_g transitions [13]. Assuming that the halogens are lower than oxygen and nitrogen ligands in the electrochemical series [24], the former transition, ³B_{1g} → ³B_{2g}, is assigned to 10 Dq^{xy} and the latter one, ³B_{1g} → ³E_g, is used to calculate the ligand field of the axial group Dq^z, from the relation [25], Dq^z = (2ν₁ - 10 Dq^{xy})/10.

The in-plane field strength 10 Dq^{xy} given in Table VII is compatible with the values recorded for complexes [NiO₄X₂] and [NiN₄X₂] [26]. The axial strength Dq^z calculated was found to be in the sequence Cl⁻ > Br⁻ > NCS⁻, similar to those reported for other complexes having the same donor atoms [27]. The parameters Dt, DT, DQ, DQ^{xz} and DQ^z have been calculated using an NSH Hamiltonian [27], and are given in Table VII. The ratio DT/DQ provides a measure of the tetragonal distortion and the values for the present complexes lie in the 0.110–0.062 range, thereby showing the complexes to be moderately distorted and the extent of the distortion to be in the order NCS⁻ > Br⁻ > Cl⁻.

The electronic absorption spectra of [NiL₃]X₂ and [NiL'₃]X₂, X = ClO₄⁻ or BF₄⁻ are given in Table VIII. The spectra exhibit bands similar to those re-

ported for octahedral nickel(II). The calculated ligand field parameters for these complexes are given in Table VIII, and are consistent with NiN₃O₃ chromophore.

Palladium(II) and iron(II) complexes

The interaction of palladium(II) salts with L or L' afforded 1:1 and 1:2 complexes, Table I. All complexes are diamagnetic, as expected for square planar d⁸ metal complexes. The molar conductivity as 10⁻³ M in MeNO₂ indicates that these complexes are non-electrolytes [28]. The solid reflectance spectra of these complexes are similar to their MeNO₂ solution spectra and exhibit bands characteristic of square planar palladium(II) complexes [29, 30]. Three d–d spin-allowed transitions are expected according to the transitions from the three lying d-levels to the empty d_{x²-y²} orbitals. The ground state is ¹A_{1g} and excited states corresponding to the above transitions are ¹A_{2g}, ¹B_{1g} and ¹E_g in order of increasing energy. The bands in the 25 000–22 000 cm⁻¹ range are assigned to ¹A_{1g} → ¹B_{1g} transition [29, 30]. The spectral features of these complexes and the calculated splitting parameter (Δ₁) according to Slater Condon Interelectronic Repulsion Parameters for palladium(II) complexes [31] are given in Table IX. The larger Δ₁ values for 2-picoly-l-

TABLE VIII. Magnetic Data (B.M.) and Ligand Field Parameters (cm^{-1}) of Tris(ligand)nickel(II) Complexes.

Compd.*	ν_1	ν_2	ν_3	10Dq	B'	β	Dq/B'	$-\lambda$	μ_{eff}
29	10430	16800	28080	10430	906	0.87	1.15	257	3.12
30	10400	16840	28100	10400	916	0.88	1.13	247	3.11
37	9500	16200	26200	9500	926	0.89	1.03	251	3.14
38	9510	16230	26200	9510	926	0.89	1.03	251	3.14

*Compound numbers are as in Table I.

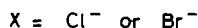
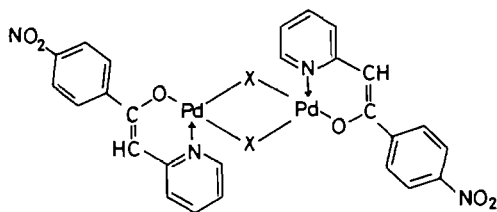
TABLE IX. Ligand Field Spectra of Palladium(II) Complexes.

Compd.*	$^1A_{1g} \rightarrow ^1B_{1g}$	C.T.	Δ_1
39	24500	30000	26600
40	24200	29850	26300
41	24380	30100	26470
42	24170	30000	26241
43	24000	29500	26100
46	22200	29280	24300
47	21200	29500	23200
48	22400	29220	24500
49	22030	30000	24120

*Compound numbers are as listed in Table I.

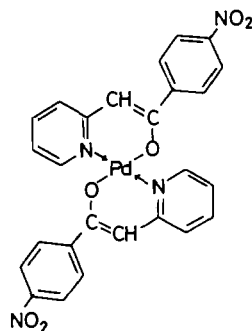
nitrophenyl ketone containing complexes than those containing 2-picolylyl-p-tolyl ketone are attributed to the greater basicity of the latter ligand [10].

The IR spectra of $[\text{PdLX}]_2$, $X = \text{Cl}^-$, Br^- , exhibit strong bands at 280 and 220 cm^{-1} , characteristic of bridging Cl^- and Br^- respectively [10]. According to the electronic and IR spectra of these complexes, the following structure could be assumed. This is



supported by the presence of $\nu\text{Pd}-\text{O}$ and $\nu\text{Pd}-\text{N}$, Table II. The IR spectra of the rest of the palladium(II) complexes exhibit far IR active bands, characteristic of terminal coordinated halides [10]. Furthermore, $\nu\text{Pd}-\text{Br}/\nu\text{Pd}-\text{Cl}$ lie in the range 0.78–0.80, supporting the assumed square planar symmetry. A more interesting point is the difference of the mode of chelation in $[\text{PdL}_2\text{X}_2]$ and $[\text{PdL}'_2\text{X}_2]$ from one side and $[\text{PdL}'\text{X}_2]$ from the other side. In the first two complexes no $\nu\text{Pd}-\text{O}$ was traced, while $\nu\text{Pd}-\text{N}$ is exhibited at 485–475, Tables II and III. Accordingly the ligands act as monodentate,

coordinated to the palladium(II) *via* the heterocyclic nitrogen atom. In complexes of stoichiometry, $[\text{PdL}'\text{X}_2]$, the ligand coordinates to the metal ion *via* the heterocyclic nitrogen and the carbonyl oxygen atoms. This is further supported by the appearance of IR active bands at 290–296 and 475–490 cm^{-1} due to $\nu\text{Pd}-\text{O}$ and $\nu\text{Pd}-\text{N}$ vibrational modes respectively [10, 29], Tables II and III. In the case of $[\text{PdL}_2] \cdot 3\text{H}_2\text{O}$, obtained by the interaction of $[\text{PdX}_2]$, $X = \text{BF}_4^-$ or ClO_4^- with 2-picolylyl-p-nitrophenyl ketone, the moderate band at 3390 cm^{-1} due to νOH which was observed for cobalt(II) and nickel(II) complexes with the same anions and ligand is not observed, indicating the deprotonation of the enolized carbonyl. Furthermore, this palladium(II) complex is a non-electrolyte and diamagnetic, indicating a square planar structure:



The same result was obtained in another similar complex [10, 29]. This is another example of the well known fact that palladium(II) forms more stable complexes than does nickel(II) [8, 10, 29].

The room temperature magnetic moments of iron(II) complexes, $[\text{FeL}_2]\text{X}_2$, $X = \text{ClO}_4^-$ or BF_4^- , are 5.38 and 5.30 B.M. respectively, indicating high spin complexes. The reflectance spectra of these complexes exhibit intense bands at 6800 and 6775 cm^{-1} , respectively, due to $^5E \rightarrow ^5T_2$ transition characteristic of tetrahedral iron(II). This is supported by the high value of the molar absorption coefficients for this band in CHCl_3 (670 and 658 $\text{l cm}^{-1} \text{mol}^{-1}$ respectively).

Conclusion

It is known that the enolization of β -dicarbonyl compounds is exothermic and enhanced by an electron withdrawing group attached to the carbonyl carbon atoms or to the α -carbon atom [32]. Therefore, the presence of the p-nitrophenyl group attached to the carbonyl carbon atom in 2-picolylyl-p-nitrophenyl ketone leads to the higher stretching vibration frequency of the carbonyl group (1740 cm^{-1}). The electron withdrawing character of the p-nitrophenyl group is enhanced by the coordination of the metal ion to the carbonyl oxygen atom. This could be taken to answer the question why the monoketone compound can be isolated in the enolic form in its complexes in this work. This monocarbonyl compound could be considered as an interesting example in this respect.

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