Some Metal Complexes of 1,3-Di-imines

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WE report the synthesis of an extensive new series of conjugated 1,3-bidentate Schiff's bases together with the results of a preliminary investigation into their use as ligands for first row transition-metal elements.

Heating 1,1′,3,3′-tetramethoxypropane under reflux in a 1 : 2 molar ratio with the appropriate aromatic amine in aqueous ethanol containing one equivalent of hydrochloric acid yields the *NN*′-disubstituted 3-iminopropeneamine monohydrochloride (LH_2Cl).

N.m.r. spectra confirm the conjugation of the propanedi-imine system. The scalar coupling of 12 c./sec. for the α- and β-protons in dimethyl sulphoxide solution indicates the presence of the *trans–trans* form, as has been observed for malondianil and malondianil monohydrochloride.[1]

The metal complexes that have been obtained, and their u.v. and magnetic data are summarised in the Table. Heating the metal halide with the ligand hydrochloride under reflux in ethanol for some hours yields compounds containing halide and the LH moiety. Heating the metal acetate with ligand hydrochloride and potassium t-butoxide in

TABLE

Complex	R	(Methanol) mμ	ϵ(l.cm.$^{-1}$ mole.$^{-1}$)	μ(B.M. at room temp.)
$MnCl_2$ $(LH)_1$	*m*-Methylphenyl	380	$4{\cdot}20 \times 10^4$	4·24
		249	$1{\cdot}22 \times 10^4$	
$FeCl_2$ $(LH)_1$	*m*-Methylphenyl	387	$5{\cdot}46 \times 10^4$	3·60
		248	$1{\cdot}36 \times 10^4$	
$CoCl_3$ $(LH)_1$	*m*-Methylphenyl	390	$1{\cdot}03 \times 10^5$	4·63
		249	$2{\cdot}70 \times 10^4$	
$CuCl_2$ $(LH)_2$	*m*-Methylphenyl	390	$3{\cdot}99 \times 10^4$	0·45
		249	$1{\cdot}50 \times 10^4$	
$ZnCl_2$ $(LH)_1$	*m*-Methylphenyl	378	$3{\cdot}87 \times 10^4$	—
		248	$1{\cdot}18 \times 10^4$	
CoL_2	*m*-Methylphenyl	521	$2{\cdot}39 \times 10^3$	
		396	$3{\cdot}81 \times 10^4$	3·84
		252	$2{\cdot}32 \times 10^4$	
NiL_2	*m*-Methylphenyl	530	$3{\cdot}09 \times 10^3$	
		396	$2{\cdot}85 \times 10^4$	3·17
		248	$3{\cdot}09 \times 10^4$	
CuL_2	*m*-Methylphenyl	Insoluble		2·07
$CoCl_3$ $(LH)_2$	*o*-Methylphenyl	360	$8{\cdot}78 \times 10^4$	4·81
		242	$1{\cdot}94 \times 10^4$	
$CuCl_2$ $(LH)_2$	*p*-Methylphenyl	394	$8{\cdot}89 \times 10^4$	0·68
		290	$9{\cdot}76 \times 10^3$	
CuCl L_1	*p*-Methylphenyl	400	—	1·27
		270		
CoL_2	*p*-Methylphenyl	522	$2{\cdot}91 \times 10^3$	
		400	$4{\cdot}04 \times 10^4$	4·28
		254	$2{\cdot}35 \times 10^4$	
NiL_2	*p*-Methylphenyl	505	$5{\cdot}0 \times 10^3$	3·17
		398	$1{\cdot}37 \times 10^4$	

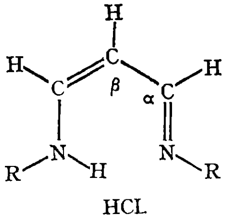
ethanol, for up to twelve hours under reflux, yields compounds containing de-protonated ligand. Elemental analyses are consistent with the above formulations.

The i.r. spectra of the complexes containing de-protonated ligand show no absorption between 3100 and 3500 cm.$^{-1}$ and have one sharp, strong absorption at 1580 cm.$^{-1}$[1,2] Complexes containing protonated ligand have two broad, strong bands at 1630 and 1590 cm.$^{-1}$ Partial deuteriation suggests that both these bands contain a large contribution from the -N–H bending mode.

FIGURE

R =

o-methoxyphenyl
o-methylphenyl
m-methylphenyl
p-methylphenyl
p-ethylphenyl
p-1-methylphenyl-n-propyl
p-n-butylpheny
p-chlorophenyl
1-naphthyl
1-anthryl
1-anthraquinonyl



[LH_2Cl]

The high intensity *d*—*d* bands of the nickel and cobalt complexes containing de-protonated ligand indicate a non-centrosymmetric ligand field. These compounds display very large contact shifts of up to 30,000 cycles at 60 Mc./sec. The line-widths, particularly for the protons of the R-group, are reasonably narrow for a paramagnetic system, ranging from 5—40 c./sec.[3]

This work is of interest for three reasons. The magnetic moments of the complexes containing protonated ligand are anomalous.[4] The flexibility of the ligand synthesis enables complicated groups to be substituted at nitrogen. Subsequent chelation to nickel and cobalt, followed by study of the contact-shifted, now first-order, n.m.r. spectra, could provide valuable structural data concerning the *N*-substituted group. Finally, the synthetic method can be readily adapted to give cyclic and non-cyclic tetradentate nitrogen-donor ligands. Initial results suggest that we have been successful in preparing such molecules.

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