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Metal Complexes of Tridentate Hybrid Ligands. IV. Cobalt Complexes of Ligands Containing the Donor Sequence As-N-N (heterocyclic)

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The compounds obtained by the interaction of four new hybrid tridentate ligands, each containing the donor sequence As-N-N, with cobalt(II) salts is described. The four ligands were obtained by the Schiff base condensation of an o-dialkylarsinoaniline and either pyridine-2-aldehyde or 6-methylpyridine-2-aldehyde.

Cobalt(II) compounds of the type $[Co(ligand)_2]Y_2$ *(where Y = I, ClO_4 or BPh_4) were obtained for all four ligands, but for the two ligands with blocking 6-methyl-groups upon the pyridine ring, where Y = NO_3, compounds of this type could not be isolated, only mono-compounds of type Co ligand $(NO_3)_2$ being obtained.*

Cobalt(II) iodide reacted with all four ligands to yield either a mono- or a bis-ligand complex. On the other hand cobalt(II) chloride, bromide or thiocyanate yielded only 1:1 ligand:cobalt compounds of the two types Co ligand X_2 and $[Co(ligand)_2][CoX_4]$. Cobalt(II) iodide complexes of this latter type were also obtained in some instances.

Physical measurments were undertaken to ellucidate the stereochemistry of the compounds, and in certain cases of anomalous magnetic moments, temperature dependent studies were carried out.

Introduction

Previous papers reported on the complexes formed by nickel(II) and cobalt(II) salts with hybrid tridentates with the donor atom sequences of As-N-O[1], As-N-S[2] and As-N-N[3]; all the ligands being derived from Schiff base reactions of o-dialkylarsinoanilines and suitable aldehydes.

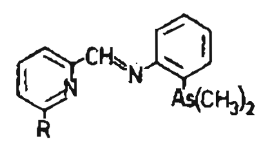
We now report the results of a study of the cobalt complexes of the four new As-N-N (heterocyclic) hybrid tridentate ligands:

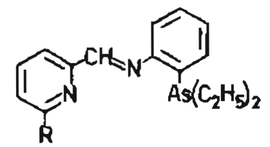
(i) 1-(2′-pyridyl)-2-(*o*-dimethylarsinobenzene)-2-azaethene (I; NNAs).

(ii) 1-(6′-methyl-2′-pyridyl)-2-(*o*-dimethylarsinobenzene)-2-azaethene (II; MeNNAs).

(iii) 1-(2′-pyridyl)-2-(*o*-diethylarsinobenzene)-2-azaethene (III; NNAsEt).

(iv) 1-(6′-methyl-2′-pyridyl)-2-(*o*-diethylarsinobenzene)-2-azaethene (IV; MeNNAsEt).





R = H NNAs I
R = Me MeNNAs II

R = H NNAsEt III
R = Me MeNNAsEt IV

Bis-ligand complexes of cobalt(II), $[CoL_2]L_2$. Bis-ligand cobalt(II) complexes of ligands NNAs(I), MeNNAs(II), NNAsEt(III) and MeNNAsEt(IV) with the anions iodide, nitrate, perchlorate and tetraphenylborate were prepared. They have the general formula $[CoL_2]Y_2.nH_2O$ (Table I).

The perchlorate salts can be readily obtained from the interaction of cobalt(II) perchlorate and the appropriate ligand. Both the perchlorate and tetraphenylborate compounds were also prepared by the addition of a solution of sodium perchlorate or tetraphenylborate to the solution of the appropriate cobalt(II) salt and the ligand. It should be noted that the bis-ligand complexes of both cobalt(II) perchlorate and tetraphenylborate are obtained in ethanol irrespective of the molar ratio (0.6-3.0) of the ligand to cobalt(II) salt used in preparation.

The interaction of equimolecular quantities of cobalt(II) nitrate with any of the ligands I-IV leads to the formation of either the mono-ligand complexes or the bis-ligand complexes depending on the nature of the ligands. Ligands I and III give rise to the bis-ligand complexes $[CoL_2](NO_3)_2nH_2O$ (L = I or III), whereas ligands II and IV always give the mono-ligand complexes of type $CoL(NO_3)_2$. This situation also occurs for the corresponding nickel(II) nitrate complexes.[4]

The fact that ligands II and IV have methyl groups at the 6-position of the pyridine ring and readily give with metal nitrates only the mono-ligand complex

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(1) B. Chiswell and K.W. Lee, *Aust. J. Chem.*, *22*, 2315 (1969).

(2) B. Chiswell and K.W. Lee, *Inorg. Chim. Acta*, *6*, 583 (1972).

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(4) B. Chiswell and K.W. Lee, *Inorg. Chim. Acta*, accepted for publication.

Table 1. Analytical Data and Preparation Mtehods for Cobalt(II) Complexes

Complex		Analysis (%)				Method of prepn.[b]
		C	H	N	Co	
Cobalt(II)-NNAs(I)						
$[Co(NNAs)_2][CoCl_4]$	Found	40.4	4.0	6.8	13.8	E
	Calc.	40.3	3.6	6.7	14.1	
$[Co(NNAs)_2][CoCl_4]2H_2O$	Found	39.1	3.8	6.6	13.7	E
	Calc.	38.8	4.0	6.5	13.6	
$[Co(NNAs)_2][CoBr_4]3H_2O$	Found	31.7	3.2	5.1	11.2	E
	Calc.	31.6	3.4	5.3	11.1	
$[Co(NNAs)_2][CoI_4]EtOH$	Found	28.9	2.8	4.4	9.5	E + LiI
	Calc.	29.2	2.9	4.5	9.6	
$[Co(NNAs)_2][Co(NCS)_4]$	Found	41.1	3.5	12.6		E
	Calc.	41.4	3.3	12.1		
$[Co(NNAs)_2][Co(NCS)_4]MeOH$	Found	41.6	3.6	11.5	12.2	E-R(Me)
	Calc.	41.4	3.6	11.7	12.3	
$Co(NNAs)_2I_2$	Found	38.6	3.6	6.2	6.6	EB
	Calc.	38.0	3.4	6.3	6.7	
$Co(NNAs)_2(NO_3)_22H_2O$	Found	42.4	4.3	10.8	7.6	E
	Calc.	42.5	4.3	10.6	7.5	
$Co(NNAs)_2(ClO_4)_2H_20$	Found	39.7	4.0	7.0		E(Cl + ClO_4
	Calc.	39.6	3.8	6.6		
$Co(NNAs)_2(ClO_4)_23H_2O$	Found	38.0	3.7	6.4	6.8	E
	Calc.	38.0	4.1	6.3	6.7	
$Co(NNAs)_2(BPh_4)_2\frac{1}{2}H_2O$	Found	71.6	5.6	4.6	4.6	E/2E/3E
	Calc.	71.5	5.6	4.4	4.6	
$[Co(NNAs)(NAs)(OH)][CoCl_4]$	Found	34.5	3.8	6.5	18.7[a]	E-R(Me,E)
	Calc.	34.7	3.7	5.5	18.7[a]	
$[Co(NNAs)(NAs)(OH)][CoBr_4]EtOH$	Found	28.9	3.2	4.8	33.6[a]	E-R(Me,E)
	Calc.	28.5	3.3	4.3	33.6[a]	
$Co(NNAs)I_2EtOH$	Found	29.7	3.3	3.5	9.4	E
	Calc.	29.7	3.3	4.3	9.1	
$Co(NNAs)I_22EtOH$	Found	31.2	3.7	4.1	8.8	E-f
	Calc.	31.3	4.0	4.1	8.5	
$Co(NNAs)(NCS)_2H_2O$	Found	40.3	3.5	11.7	11.8	E-R(Me,E)-f
	Calc.	40.0	3.6	11.7	12.3	
$Co(MeNNAs)Cl_2$	Found	42.3	4.2	6.6	13.6	E-R(EMe)
	Calc.	41.9	4.0	6.5	13.7	
$Co(MeNNAs)Br_2$	Found	34.4	3.4	5.6		E-R(EMe)
	Calc.	34.7	3.3	5.4		
$Co(MeNNAs)I_2EtOH$	Found	31.4	3.2	4.8		E
	Calc.	31.0	3.5	4.3		
$Co(MeNNAs)(NO_3)_2$	Found	37.1	3.6	11.5	12.1	E
	Calc.	37.1	3.5	11.6	12.1	
$Co(MeNNAs)_2I_2$	Found	39.1	4.0	6.0	6.1	EB-f
	Calc.	39.4	3.8	6.1	6.4	
$Co(MeNNAs)_2I_2EtOH$	Found	40.3	4.3	5.6	5.9	E
	Calc.	40.0	4.2	5.8	6.2	
$Co(MeNNAs)_2I_23H_2O$	Found	37.6	4.0	5.7	5.9	E-f
	Calc.	37.4	4.2	5.8	6.1	
$Co(MeNNAs)_2(ClO_4)_2$	Found	41.6	4.1	6.6	6.8	E
	Calc.	41.9	4.0	6.5	6.8	
$Co(MeNNAs)_2(BPh_4)_2$	Found	72.2	5.9	4.3	4.4	E/2T/3E
	Calc.	72.2	5.8	4.3	4.5	
$[Co(MeNNAs)_2][CoCl_4]3H_2O$	Found	39.4	3.9	6.3		E-R(Me,E)
	Calc.	39.4	4.4	6.1		
$[Co(MeNNAs)_2][Co(NCS)_4]$	Found	43.1	4.0	11.5		E
	Calc.	42.9	3.6	11.9		
$[Co(MeNNAs)_2][Co(NCS)_4]H_2O$	Found	42.6	3.9	11.3	11.9	E
	Calc.	42.1	3.7	11.5	12.2	
$[Co(MeNNAs)_3][CoCl_4]$	Found	43.7	4.7	6.3	13.4	2EB-f-Hp
	Calc.	43.1	4.3	6.3	13.2	
$[Co(MeNNAs)_3][CoCl_4]2EtOH$	Found	44.6	4.7	6.0	12.0	EB
	Calc.	44.0	5.1	5.7	12.0	
$[Co(MeNNAs)_2][CoBr_4]4H_2O$	Found	33.7	3.7	4.9	10.5	E-f + $LiBr_2$
	Calc.	33.7	4.0	4.9	10.3	
$[Co(MeNNAs)_2][CoI_4]$	Found	30.4	3.1	4.3	9.5	0.6EB + LiI_2
	Calc.	30.6	3.0	4.5	9.4	
$[Co(MeNNAs)_3][Co(NCS)_4]$	Found	44.3	4.1	11.2	12.2	EB
	Calc.	44.1	3.9	11.4	12.1	
$[Co(MeNNAsI]I\frac{1}{2}C_6H_6\frac{1}{2}H_2O$	Found	33.6	3.5	4.6	8.5	EB
	Calc.	33.7	3.6	4.2	8.7	
$[Co(MeNNAsI]I$	Found	30.3	3.2	4.4	9.3	E-f-R(E)
	Calc.	30.6	3.0	4.5	9.4	
$Co(NNAsEt)_2I_2H_2O$	Found	39.8	4.0	5.6	6.1	1.5EBHp
	Calc.	40.0	4.2	5.8	6.1	

Table II. (Continued).

$Co(NNAsEt)_2(NO_3)_2\frac{1}{2}H_2O$	Found	56.7	4.9	10.3	7.5	2E
	Calc.	56.8	4.8	10.2	7.2	
$Co(NNAsEt)_2(NO_3)_2 1\frac{1}{2}H_2O$	Found	45.8	4.5	10.0	7.0	EB-f
	Calc.	45.8	4.9	10.0	7.0	
$Co(NNAsEt)_2(ClO_4)_2H_2O$	Found	42.2	4.5	6.0	6.4	$E(NO_2+ClO_4)$
	Calc.	42.1	4.5	6.1	6.5	
$Co(NNAsEt)_2(ClO_4)_2$	Found	43.3	4.5	6.5	6.5	E
	Calc.	43.3	4.3	6.3	6.7	
$Co(NNAsEt)_2(BPh_4)_2$	Found	72.0	6.0	4.0	4.3	$E(NO_2+BPh_4)$
	Calc.	72.4	5.9	4.2	4.5	
Cobalt(II)-MeNNAsEt(IV)						
$Co(MeNNAsEt)Cl_2$	Found	44.3	4.6	6.1	12.9	E
	Calc.	44.5	4.6	6.1	12.8	
$Co(MeNNAsEt)Br_2$	Found	37.6	4.0	5.1	10.7	0.8E
	Calc.	37.3	3.8	5.1	10.8	
$Co(MeNNAsEt)I_2$	Found	31.9	3.5	4.5	9.0	E
	Calc.	31.8	3.3	4.4	9.2	
$Co(MeNNAsEt)(NCS)_2$	Found	45.5	4.3	11.0	11.6	E
	Calc.	45.2	4.2	11.1	11.6	
$Co(MeNNAsEt)(NO_3)_2$	Found	39.9	4.2	11.0	11.6	E
	Calc.	39.9	4.1	10.9	11.5	
$Co(MeNNAsEt)_2I_2$	Found	42.0	4.4	5.9	6.1	$2E/E(NO_2+I)$
	Calc.	42.1	4.3	5.8	6.1	
$Co(MeNNAsEt)_2(ClO_4)_2$	Found	44.7	4.7	6.1	6.4	$E/E(I+ClO_4)$
	Calc.	44.6	4.6	6.1	6.5	
$Co(MeNNAsEt)_2(BPh_4)_2H_2O$	Found	71.9	6.3	4.0	4.3	$2E(NO_2+BPh_4)$
	Calc.	71.8	6.1	4.1	4.3	

[a] Content of halide (%). [b] See experimental section.

rather than the bis-ligand complex, leads to the conclusion that the methyl group at the 6-position exerts a considerable steric hindrance to the chelation of a further ligand, but does not affect the coordination of less bulky ligands such as nitrate ion.

Ethyl groups attached at the arsenic donor atoms of ligand III and IV seem to exert no appreciable steric effect as shown by the fact that ligand III reacts with an equimolecular quantity of cobalt(II) or nickel (II)[4] nitrate to give only bis-ligand complexes.

The interaction of cobalt(II) iodide and any of the ligands I-IV gives rise to the formation of both mono- and bis- ligand complexes for each ligand. The bis-ligand complexes are much less soluble in ethanol than the corresponding mono-ligand compounds, and can be obtained by preferential precipitation. When two or more molecular quantities of ligand per cobalt iodide are used, the bis-ligand complexes are always obtained.

All the bis-ligand complexes obtained are crystalline and stable in air showing no sign of oxidation after several months in contact with dry air. Most of them are practically insoluble in ethanol or benzene, and soluble in chloro- or nitro-derivative solvents such as nitromethane and chloroform.

The values of molar conductivities for these bis-ligand complexes are those of typical 1:2 electrolytes in nitromethane and in nitrobenzene, while the infrared spectra of the anions, nitrate and perchlorate exhibit a very strong band at ca. 1360 cm^{-1} and 1090 cm^{-1}, respectively, which are characteristic of the corresponding uncomplexed, ionic anions. (The data are listed in Table IV, along with the assignments). On the basis of physical properties of the bis-ligand complexes they are all octahedral complexes. Their magnetic properties in the solid state, and their electronic spectra will be discussed separately.

Magnetic properties of bis-ligand complexes. The magnetic moments of the bis-ligand complexes measured at room-temperature are shown in Table II. Of the compounds $Co(MeNNAsEt)_2Y_2$ ($Y = I, ClO_4, BPh_4.1/2H_2O$) prepared from ligand IV, the tetraphenylborate compound is essentially of the low-spin type with a magnetic moment of 1.98 B.M. at room temperature, whilst the magnetic moments of the corresponding iodide and perchlorate compounds are 2.50 and 3.82 B.M. respectively. Both the iodide and perchlorate complexes do not obey the Curie-Weiss law; instead the complexes display anomalous magnetic behaviour (see Table III). The plots of μ_{eff} and $1/\chi_M$ against T for these two compounds over the temperature range 80-293°K are shown in Figure 1.

If the low moments were due only to the presence

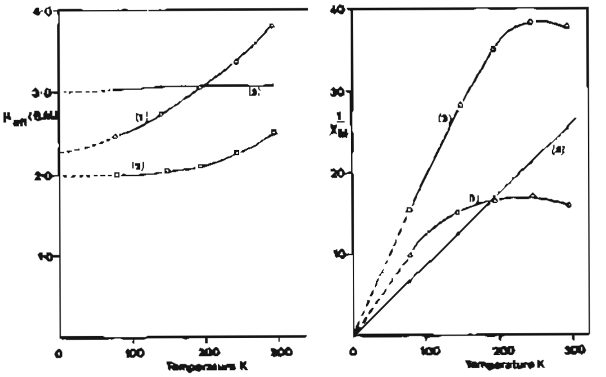

Figure 1. Variation of μ_{eff} and $1/\chi_M$ for $Co(MeNNAsEt)_2Y_2$ with temperature. (1) $[Co(MeNNAsEt)_2](ClO_4)_2$. (2) $[Co(MeNNAsEt)_2]I_2$. (3) $Co(NNAs)I_2EtOH$.

Table II. Magnetic susceptibility data of bis-ligand complexes of Cobalt(II)

Complex	T°K	$10^6\chi_g$	$10^6\chi_M'$	μ_{eff} (B.M.)
$Co(NNAs)_2I_2$	295.3	1.29	1554	1.90
$Co(NNAs)_2(NO_3)_2 2H_2O$	259.3	2.31	2200	2.28
$Co(NNAs)_2(ClO_4)_2H_2O$	295.3	1.30	1500	1.89
$Co(NNAs)_2(ClO_4)_2 3H_2O$	296.6	1.30	1523	1.92
$Co(NNAs)_2(BPh_4)_2 \frac{1}{2}H_2O$	299.3	1.10	2101	2.25
$Co(MeNNAs)_2I_2$	295.3	1.36	1653	1.97
$Co(MeNNAs)_2I_2EtOH$	296.3	1.12	1470	1.89
$Co(MeNNAs)_2I_2 3H_2O$	296.3	3.42	3773	3.01
$Co(MeNNAs)_2(ClO_4)_2$	301.8	1.57	1760	2.07
$Co(MeNNAs)_2(BPh_4)_2$	299.3	0.94	1926	2.15
$Co(NNAsEt)_2I_2H_2O$	295.3	0.96	1427	1.86
$Co(NNAsEt)_2(NO_3)_2 \frac{1}{2}H_2O$	295.3	1.92	1810	2.08
$Co(NNAsEt)_2(ClO_4)_2H_2O$	295.3	1.21	1513	1.90
$Co(NNAsEt)_2(ClO_4)_2$	294.3	0.94	1245	1.73
$Co(NNAsEt)_2(BPh_4)_2$	295.3	0.46	1323	1.78
$Co(MeNNAsEt)_2I_2$	293.0		2630	2.48*
	296.3	2.23	2620	2.51
$Co(MeNNAsEt)_2(ClO_4)_2$	293.0		6248	3.83*
	296.3	5.68	5645	3.67
$Co(MeNNAsEt)_2(BPh_4)_2H_2O$	294.8	0.64	1641	1.98

* measured by Faraday Method (sec Table IV).

Table III. Magnetic moments of $[Co(MeNNAsEt)_2]Y_2$ at various temperatures *

Temp.	10 Amp.		20 Amp.	
°K	χ_M'	μ_{eff} (B.M.)	χ_M'	μ_{eff} (B.M.)
(A) $Co(MeNNAsEt)_2(ClO_4)_2$				
293	6226	3.819	6248	3.825
243	5799	3.356	(6433)	3.535
193	5994	3.041	6079	3.063
143	6491	2.724	6597	2.746
77	9907	2.469	10023	2.484
(B) $Co(MeNNAsEt)_2I_2$				
293	2708	2.518	2630	2.482
243	2613	2.253	2601	2.248
193	2843	2.094	2840	2.093
148	3523	2.042	3541	2.047
77	6385	1.982	6458	1.994

* measured by Faraday method.

of some cobalt(II) species, such a mixture should show normal Curie-Weiss behaviour.[5] On the basis of the analytical data and the deviation from Curie-Weiss law of these compounds, the existence of a mixture of cobalt(III) complex with high-spin cobalt(II) complex is precluded. The possible presence of ferromagnetic impurities in the compounds is also excluded by the magnetic field-strength independence of the observed magnetic susceptibilities.

The temperature-dependence of the magnetic moments of the cobalt(II) complexes, $Co(MeNNAsEt)_2Y_2$ (X = I, ClO_4), and the shape of the curve, $1/\chi_M$ against T, suggest that the anomalous magnetic behaviour is a result of a thermal equilibrium between the doublet ground state (^2E) and a thermally accessible quartet state ($^4T_1$).

If one takes as the high-spin and low-spin limits the values of 5.0 B.M. and 2.0 B.M., the percentage of high-spin form in the iodide and perchlorate compounds, $[Co(MeNNAsEt)_2]Y_2$, at 293°K is about 10% and 50%, respectively.

The fact that the ligands I-IV have the same donor sequence N-N-As and that the cobalt(II) complexes of ligands, I, II and III approximate to spin-paired behaviour at room temperature, while the corresponding cobalt(II) complexes of the ligand IV (MeNNAsEt) are in thermal equilibria between two spin states, leads to the conclusion that the anomalous magnetic moments of the complexes of ligand IV, $[Co(MeNNAsEt)_2]^{2+}$ are presumably due to the modification of ligand shape.

Molecular models of the bis-ligand complexes formed by the ligands I, II or III do not show significant steric hindrance. However, in the complex of ligand IV, $[Co(MeNNAsEt)_2]^{2+}$, the molecular model shows significant inter-ligand steric hindrance, with the methyl group at the 6-position of the pyridine ring blocking the free rotation of an ethyl group attached to the arsenic atom of the second ligand moiety.

This inter-ligand steric interaction could lead to a concomitant increase in the cobalt-ligand distance in the complex $[Co(MeNNAsEt)_2]Y_2$ (Y = I, ClO_4). Such an increase in the metal-ligand distance will lead to a decrease in the ligand field strength (Δ) possibility accompanied by shifting of the ground state of the compound from the low-spin ^2E state to the high spin $^4T_1$ state.

A similar situation, the conversion of a low-spin complex into the high-spin analogue by the lengthening of the metal-ligand bond caused by the steric requirements of the ligand, has been observed for similar cobalt(II) complexes with tridentate ligands with donor atom sets of the type SNN.[5]

Electronic spectra of low-spin octahedral cobalt(II) compounds. The reflectance spectra of the bis-ligand complexes were recorded over the range 12.0 to 25.0 kK. They exhibit very intense, but poorly resolved peaks, and on the basis of the absorption pattern, they can be classified into two classe:

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(5) P.S.K. Chia and S.E. Livingstone, *Aust. J. Chem.*, 22, 1826, (1969).

Table IV. Infrared spectral data of anions in cobalt(II) complexes.

Thiocyanate	ν(C-N)	δ(NCS)	ν(Co-NCS)
$[Co(NNAs)][Co(NCS)_4]$	2068vs br	480m	308vs br
$[Co(NNAs)_2][Co(NCS)_4]EtOH$	2065vs br	480m	308vs br
$[Co(NNAsEt)_2][Co(NCS)_4]$	2062vs br	480m	308vs br
$[Co(MeNNAs)_2][Co(NCS)_4]$	2062vs br	480m	308vs br
$Co(MeNNAsEt)(NCS)_2$	2118s sp 2086vs	470m 475sh	
$K_2[Co(NCS)_4]$	2058-2079vs		
$(Cat)_2[Co(NCS)_4]$(ref. 202a 206)	~2065vs br	481w	303-311vs br
Nitrate	ν_3 (cm^{-1})	ν_2 (cm^{-1})	$\nu_1+\nu_3$ (cm^{-1})
$Co(NNAs)(NO_3)_2 2H_2O$	1350vs br	830m sp	2370w
$Co(NNAsEt)_2(NO_3)_2 \frac{1}{2}H_2O$	1345vs br	830m sp	2370w
Perchlorate	ν_3 (cm^{-1})	ν_2 (cm^{-1})	
$Co(NNAs)_2(ClO_4)_2$	1090vs br	625s sp	
$Co(NNAsEt)_2(ClO_4)_2$	1090vs br	624s sp	
$Co(MeNNAs)_2(ClO_4)_2$	1090vs br	624s sp	
$Co(MeNNAsEt)_2(ClO_4)_2$	1090vs br	625s sp	

Cat = Me_4N, Et_4N, Ph_3BuP etc. Intensity: vs very strong, sp sharp, m medium, sh shoulder, s strong, br broad, w weak.

(i) The greenish-brown cobalt(II) complexes containing the ligands NNAs and NNAsEt display a broad shoulder at approx. 15.5, two bands at approx. 17.5 and 19.0 kK and a more intense band at approx. 23.0 kK.

(ii) The corresponding brown complexes containing the ligands MeNNAs and MeNNAsEt exhibit bands at 12.5 kK, 16.5-18.0 kK and 20.22 kK.

The spectral study of these bis-complexes in nitromethane solution appears not to give reliable data; all complexes in purified nitromethane solution give rise to an at first deep brown solution, but this slowly changes to a green solution even in an inert atmosphere. The rate of colour change in nitromethane solution is much faster in the complexes containing ligands I and III than in the corresponding complexes of ligands II and IV. When the solution spectra of the bis-complexes were recorded immediately after dissolution in nitromethane, the resulting spectra displayed a similar pattern to those of the corersponding solid state spectra.

The changes in the solution spectrum of one compound, $[Co(NNAsEt)_2](ClO_4)_2$, were studied over a period of time (Figure 2). The freshly prepared brown solution displayed three absorption bands at 14.5, 16.00 and 18.0 kK. The band at 14.5 kK did not change appreciably with time, whilst the last two bands decreased in intensity with time and completely disappeared in approx. 20 hours, to finally give a green solution with an absorption band at 14.5 kK. On standing for more than two weeks, this green solution changed into an orange- brown solution exhibiting an absorption maximum at 20.0 kK, which is probably due to a square- planar cobalt(II) entity or cobalt(III) complex formed by the air oxidation of the cobalt(II) complex.

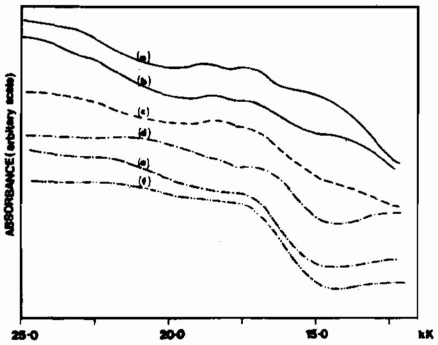

Figure 2. The change in spectrum of $Co(NNAsEt)_2(ClO_4)_2$ in nitromethane solution with time. Concentration $1.23\times 10^{3}M$ in $MeNO_2$. Elapsed time: (a) fresh solution (2 min), (b) 10 min, (c) 20 min, (d) 50 min, (e) 95 min, (f) 4 weeks ($2.62\times 10^{-3}M$).

It is worth noting that a similar absorption intensity change has been observed even in the solid state for $[Co(terpyridine)_2]Y_2$ in KBr pellets.[6] It should be noted that the bis-complexes containing ligand I or III, and II or IV in the aged solution exhibit their absorption maxima at ~15.0kK and ~12.5kK, respectively. The most notable feature of the various solid and freshly prepared solution spectra studied in this investigation, is their great similarity to those of the bis-2,2,'2″-terpyridyl,[6] cobalt(II) complexes.

Cobalt(II) complexes of the type $[CoL_2][CoX_4]$. The interaction of equimolecular quantities of cobalt(II) halides or thiocyanate with the ligand NNAs(I) and NNAsEt(III) in an inert atmosphere leads to the formation of dark green crystals of the empirical formula $CoLX_2$ (L = NNAs, NNAsEt; X = Cl, Br, I, NCS) (the iodide complexes have a dark brown colour). It appears that these compounds should be assigned the general formula $[CoL_2][CoX_4]$ (Table I). Thus, their magnetic moments can be explained on the basis of a low-spin octahedral cation (μ_{eff} = 1.80 -2.07) and a tetrahedral anion. Conductivity measurements in nitrobenzene and nitromethane support this formation while the presence of the tetrahedral anion is substantiated by typical $[CoX_4]$ electronic absorption peaks.

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(6) S.J. Judge and W.A. Baker Jr., *Inorg. Chim. Acta*, *1*, 68, (1967).

Table V. Magnetic susceptibility data of mono-ligand complexes of Cobalt(II)

Complex	T°K	$10^6\chi_g$	$10^6\chi_M'$	μ_{eff} (B.M.)
Co(MeNNAs)Cl_2	296.3	20.2	8822	4.60
Co(MeNNAs)Br_2	298.0	17.21	9172	4.68
Co(MeNNAs)I_2EtOH	297.3	16.60	11260	5.18
Co(MeNNAs)$(NO_3)_2$	301.7	16.95	8407	4.52
Co(MeNNAsEt)Cl_2	294.3	19.05	8960	4.57
Co(MeNNAsEt)Br_2	294.3	15.80	8932	4.60
Co(MeNNAsEt)I_2	294.3	14.50	9620	4.78
Co(MeNNAsEt)$(NCS)_2$	294.3	17.14	8885	4.58
Co(MeNNAsEt)$(NO_3)_2$	294.3	16.35	8601	4.52
[Co(NNAs)I]IEtOH	293.0	5.57	3884	3.03
	293.0		3928	3.08*
[Co(NNAs)(NCS)](NCS)H_2O	293.0	5.70	2992	2.60*
[Co(NNAsEt)I]I½C_6H_6½H_2O	296.3	3.34	2581	2.48
[Co(NNAsEa)I]I	296.3	4.95	3392	2.84

* measured by Faraday Method

Under the same conditions the ligands II and IV give rise to greenish-brown mono-ligand complexes which will be discussed in the next section. However ligand II forms a green complex with cobalt(II) thiocyanate similar to the green thiocyanate complexes formed by ligands I and III above.

Attempts to recrystallize the complexes [Co(NNAs)$_2$] [CoX_4] (X = Cl, Br) in air in methanol-ethanol solutions leads to the formation of the partially hydrolibed bright green cobalt(III) and cobalt(II) complexes of formula [Co(NNAs)(NAs)(OH)] [CoX_4] (NAs = o-dimethylarsinoaniline).

All the green complexes are crystalline and stable for a long time when stored in a dry atmosphere. They are moderately soluble in nitromethane.

Mono-ligand cobalt(II) complexes CoLX_2. It has already been noted that the brown complexes of the empirical formula CoLX_2 (L = MeNNAs, MeNNAsEt; X = Cl, Br, I, NO_3) and Co(MeNNAsEt) $(NCS)_2$ were obtained by the interaction of equimolecular quantities of the appropriate cobalt(II) salt and ligand in ethanol solution (Table I). They are moderately soluble in most common organic solvents containing nitro- or chloro- groups, such as chloroform and nitromethane, producing greenish-brown solutions.

The complexes Co(MeNNAs)X_2 (X = Cl, Br) were recrystallized from ethanol-methanol solution in open air, and there is no evidence at all for the hydrolysis of the ligand or oxidation of the cobalt(II) atom in the recrystallized complexes.

The magnetic moments measured at room temperature are listed in Table V. The complexes formed by the ligand MeNNAs and MeNNAsEt are all of the high-spin type with magnetic moments ranging from 4.52 to 4.78 B.M. except for one iodide compound (5.18 B.M.), whilst the iodide compounds obtained from the ligand NNAs and NNAsEt exhibit room temperature magnetic moments within the range 2.48-3.03 B.M.

The values of molar conductivity measured in ca. 10^{-3} solution in nitromethane or nitrobenzene suggest that the high-spin chloride and bromide complexes are dissociated to a small extent while the low-spin complexes are appreciably dissociated. Thus, the high-spin compounds possess $\Lambda_M < 10$ r.o. in nitromethane, while the low-spin complexes exhibit molar conductivities typical of 1:1 electrolytes (Λ_M = 64-81 $cm^2 \cdot ohm^{-1} mole^{-1}$) in nitromethane.

The diffuse reflectance spectra of the low-spin complexes (Figure 3) are different from those of low-spin octahedral, high-spin tetrahedral or five-coordinate complexes. As the complexes are univalent electrolytes in solution and the ligand is potentially tridentate, the coordination number may be four. Since the complexes are of the low-spin type, a tetrahedral structure is not possible. Furthermore, the spectral data in the visible region cannot be consistently interpreted on the basis of tetrahedral or low-spin five-coordinate structures which would be derived by bridging of the anions. On the other hand, these spectra appear to be similar to those of other low-spin cobalt(II) complexes to which a square-planar structure has been attributed. In particular the band at ca. 20-21 kK for the iodide complexes can be correlated with those at 21.7, 22.7 kK for square-planar Co$(PEt_3)_2$-$(NCS)_2$[7] and Co$(en)_2(AgI_2)_2$ (en = ethylenediamine),[8] respectively.

The magnetic susceptibility study of the complex Co(NNAs)I_2EtOH over the temperature range 77-293°K

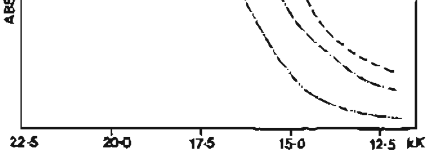

Figure 3. Reflectance spectra of the low spin mono-ligand complexes of Cobalt(II). (a) [Co(NNAsEt)I]I. (b) Co(NNAs)I_2EtOH. (c) Co(NNAs)$(NCS)_2H_2O$.

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(7) M. Nicolini, C. Pecile, and A. Turco, *Coord. Chem. Rev.*, *1*, 269 (1969).

(8) A.B.P. Lever, I. Lewis, and R.S. Nhyolm, *J. Chem. Soc.*, 2552, (1963).

indicates that the magnetic moment is almost independent of temperature (Table VI) and the Curie-Weiss law is obeyed for this compound which has the small value of the Curie-Weiss constant $\theta = +2$ (Figure 1).

Table VI. Magnetic data for Co(NNAs)I_2EtOH

°K	$10^6\chi_M$	$1/\chi_M$	μ_{eff}(.BM.)
293	3928	25.50	3.082
243	4732	21.15	3.081
293	6019	16.75	3.097
143	8117	12.40	3.095
77	14700	6.85	3.057

High-spin cobalt(II) complexes. The spectra of these high-spin complexes in the crystal field region have been measured in both the solid state (12.0-27.0 kK) and in solution (5.0-25.0 kK). The intense band which appears at 25-26 kK is probably due to charge transfer.

The reflectance spectra do not differ appreciably from those of solutions in inert solvents such as chloroform. Furthermore, the spectra of the halide complexes $CoLX_2$ (L = MeNNAs, MeNNAsEt; X = Cl, Br, I) are very similar. Small displacements of the frequencies of the maxima can be correlated with the respective positions of the halogens in the spectrochemical series. Esentially the same stereochemistry may therefore be assigned to these complexes.

The spectra of the nitrate complexes in the solid state are essentially identical for both ligands MeNNAs and MeNNAsEt, and similar in shape to those of the halide complexes. But the spectrum of the thiocyanate complex Co(MeNNAsEt)$(NCS)_2$ is different to those of the analogous halide complexes.

As these high-spin complexes with the exception of Co(MeNNAsEt)I_2 are only partially dissociated in solution and the ligands are potentially tridentate, the coordination number of cobalt(II) cannot be less than five. Furthermore, the spectral data of the halide complexes cannot be consistently interpreted on the basis of an octahedral structure, which would be achieved by the bridging of halide anion.

The spectra of the halide complexes appear to be simliar to those of other high-spin five-coordinate cobalt(II) complexes and consist of five fairly well defined bands shown below:

	NNAs* kK	M	Py(R)$_2$** kK	M	N-N$_3$*** kK	Transitions
(i)	ca. 5.3	10-16	ca. 5.0	10-14	5.7	${}^4A_2'(F)\rightarrow{}^4E'(F)$
(ii)	10-10.3	7-10	8.0-8.5	9-11	12.3	$\rightarrow{}^4E'(F)$
(iii)	12.5	14-20	11-11.5	6.5-9	12.3	$\rightarrow{}^4E'(F)$
(iv)	ca. 16	ca. 100	16.0-16.7	52-93	16.1	$\rightarrow{}^4A'_2(P)$
(v)	18.5	120-180	17.5-18.0	48-114	19.2-19.8	$\rightarrow{}^4E''(P)$

* NNAs = MeNNAs, MeNNAsEt (this work). ** Py(R)$_2$ = NN'-2,6-diacetylpyridine-dialkylimine[9]. *** N-N$_3$ = tris-(2-dimethy-l aminoethyl)amine[10].

As for other five-cordinate cobalt(II) complexes, these bands can be assigned to transitions in a field of D_{3h} symmetry. In particular, the transition which is present in the spectrum of [Co(N-N$_3$)Br]Br at 12.3 kK is very sensitive to the characteristics of the field (in the N-N$_3$ complexes of general formula [Co(N-N$_3$)X]X, it is at 13.4 kK for X = ClO_4 and at 12.20 kK for X = I). Furthermore when the symmetry of the complexes decreases, this band splits into two components, as in the complexes of the ligands N,N'-2,6-diacetyl-pyridine-dialkylimine[9], and ligands containing N-N-As donor sequence (MeNNAs and MeNNAsEt).

The spectra of the high-spin complexes studied in this work can also be correlated with those of the complexes Co(MABen-NEt$_2$) Cl_2[11] and Co (Me$_5$dien)Cl_2.[12] The latter has been shown by X-ray diffraction to have a five-coordinate structure intermediate between that of the trigonal bipyramid and the square-pyramid. The magnetic moments of the complexes fall in the range 4.5-4.8 B.M. and are comparable to those found for other high-spin cobalt(II) five-cordinate complexes.[13]

The solution spectrum of the iodide complex, Co(MeNNAsEt)I_2, in nitromethane is different to that in the solid state, exhibiting structured weak bands at 13.0-17.0 kK and an intense band at 21.5 kK. The latter band is very close to that of the low-spin square-planar cobalt(II) complexes described in the preceeding section. The value of the molar conductivity in the same solvent is indicative of a typical 1:1 electrolyte. It is therefore reasonable to assume that this iodide complex of the ligand MeNNAsEt in nitromethane solution is dissociated to form square-planar species.

The infrared spectra of nitrate in the complexes CoL$(NO_3)_2$ (L = MeNNAsEt) show no band around 1360 cm^{-1}, suggesting that all nitrate groups are bonded to the cobalt(II) atom, but their bonding modes, as either uni- or bidentate or a mixture of both, could not definitely be deduced from the infrared spectrum of the N-O stretching region, in which the corresponding halide complexes display strong bands at ca. 1290 and 1465 cm^{-1}. On the basis of the close similarity of their reflectance spectra with those of halide complexes, both the nitrate groups are presumably acting as monodentate ligands to form five-coordinate complexes. These nitrate complexes are practically nonelectrolytes in nitrobenzene but in nitromethane solution they are partially dissociated and the molar conductivities increase in dilution and on standing (Table VII), suggesting that the nitrate groups are slowly displaced by solvent molecules.

The thiocyanate complex Co(MeNNAsEt)$(NCS)_2$

(9) L. Sacconi, R. Morassi, and S. Midollini, *J. Chem. Soc.* (*A*), 1510 (1968).

(10) M. Ciampolini, N. Nardi, and G.P. Speroni, *Coord. Chem. Rev.*, *1*, 222 (1966).

(11) L. Sacconi, I. Bertini, and R. Morassi, *Inorg. Chem.*, 6, 1548 (1967).

(12) M. Ciampolini and G.P. Speroni, *Inorg. Chem.*, *45*, (1966).

Table VII. Conductivity data of Co(MeNNAsEt)(NO_3)$_2$ in nitromethane.

Concentration M	Molar conductivities fresh soln.	Λ_M, $cm^2ohm^{-1}mole^{-1}$) aged soln. (30 min.)
3.99×10^{-3}	39.5	77.1
8.57×10^{-4}	87.0	—
6.00×10^{-4}	10	178
2.07×10^{-4}	146	210

exhibits a different reflectance spectrum to those of the analogous halide and nitrate complexes, and displays a low molar conductivity ($\Lambda_M = 9.3$) in nitromethane solution. The infrared spectrum (Table IV) in the C-N stretching frequency region displays two bands at 2086 cm^{-1} (very strong) and 2118 cm^{-1} (strong and sharp), indicating that the thiocyanate groups are acting as an N-bonded terminal and a bridging group. It is therefore reasonable to assume that the complex Co(MeNNAsEt)(NCS)$_2$ has octahedral stereochemistry by the intermolecular bridging of the thiocyanate group, as has been found in the analogous nickel(II) thiocyanate complexes described in Part II.[2]

Experimental Section

General procedure for the preparation of metal complexes. The warm and deaerated ligand solution was slowly added to the appropriate hot metal salt solution (code (i)) in approx. 40 ml of absolute ethanol or mixed solvent (code (ii)).

(i) When the metal complex compound separated during refluxing of the solution for 20 min. it was digested for another 10-20 minutes and the solution was then alowed to cool to room temperature.

(ii) When the metal complex compound did not appear to separate within approx. 20 min., the solvent was slowly evaporated until crystals started to separate or evaporated to approx, 20 ml. and allowed to cool either to room temperature, or in an ice-bath.

(iii) When procedure (ii) did not yield the desired metal complex, the solution was warmed and another solvent (10-40 ml) slowly added followed by procedure (i) or (ii).

The metal complexes were collected and washed with appropriate solvents and finally with hexane. If necessary, the metal complex compounds were recrystallized from the appropriate solvent. When undesired products or impurities separated during the procedure (i), (ii) or (iii), the solution was filtered while hot.

Code (*i*). (a) The number in front of the solvent indicates mole ratio of the ligand and metal salt; no arabic number indicates 1:1 mole ratio. (b) -f: filtered while hot. (c) -R( ): recrystallized from solvents in the bracket. (d) -: change of solvent.

(ii) The code for solvents used for the preparation and the recrystallization of the complex compounds is a follows:

E	ethanol
Me	methanol
Hp	heptane
H	hexane
W	water

(iii) Examples of the codes for the preparation of metal complexes: (a) EB-f: 1:1 mole ratio of ligand and metal salt was used in a mixed solvent of absolute ethanol and benzene and filtered while hot to remove the undesired products. (b) 2E-R(Me): The complex compounds are prepared from a 2:1 mole ratio of ligand to metal salt in ethanol solution and recrystallized from methanol. (c) E(NO_3+BPh_4): A tetraphenylborate salt was added to equimolecular quantities of metal(II) nitrate and ligand in ethanol.

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(13) L. Sacconi, *J. Chem. Soc.* (*A*), 248 (1970).