

Organobridged dicobaloximes: synthesis and NMR correlation

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Abstract

Organobridged dicobaloximes of the type $\text{Py}(\text{L})_2\text{Co}^{\text{III}}-(\text{CH}_2)_n-\text{Co}^{\text{III}}(\text{L})_2\text{Py}$ [$\text{L} = \text{dmgH}^-$ and dpgH^- , $n = 3, 4, 5, 6$ and 10] are synthesized by the reaction of $\text{Co}^{\text{I}}(\text{L})_2\text{Py}$ with the corresponding alkyl dihalides. A mixture of haloalkylcobaloximes and the dicobaloxime is formed in each reaction. The purification procedure for the dicobaloxime is established. A comparison of 'cis influence' due to the equatorial ligands in the haloalkyl and the dicobaloximes by ^1H NMR reveals that the extent of the cis influence on the $\text{Co}-\text{CH}_2$ resonance is more in the case of the dicobaloxime but it is nearly same for the P_α and the P_γ resonances.

Keywords: Cobalt; Organobridged dicobaloximes; Organocobaloximes

1. Introduction

The chemistry of bis(dioximato) cobalt(III) complexes (hereafter referred to by the generic name of cobaloximes) have been explored extensively during the last three decades [1–4]. This is due to their interest as models of Vitamin B₁₂ coenzyme [2,3,5,6], as templates in organic synthesis and as catalysts in many chemical processes [7]. As small structural changes in the molecule have profound influence on the $\text{Co}-\text{C}$ bond reactivity [2], there has been a continued interest in the synthesis of new organocobaloximes [4,8]. Much of the synthesis has been limited to the use of dimethylglyoxime monoanion (dmgH^-) as the equatorial ligand [2,3,9]. A few examples of the organocobaloximes having other similar ligands¹ like gH^- , dpgH^- , chgH^- and mpgH^- are also known in the literature [5,10–17].

Surprisingly, the neutral organobridged dicobaloximes of the type $\text{Py}(\text{L})_2\text{Co}^{\text{III}}-\text{CH}_2-\text{R}-\text{CH}_2-\text{Co}^{\text{III}}(\text{L})_2\text{Py}$ are virtually unknown in the literature. The synthesis of only four complexes (where $\text{R} = \text{CH}_2$, CH_2CH_2 , $1,3-\text{C}_6\text{H}_4$ and $1,4-\text{C}_6\text{H}_4$, $\text{L} = \text{dmgH}^-$) has been mentioned by Schrauzer and Windgassen [18] and Johnson and coworkers [19] but no spectral character-

istics were given for these complexes. Besides, we always got a mixture of haloalkylcobaloxime and the dicobaloxime following their procedure.

We believe that these complexes are interesting not only from the synthesis point of view but also the orientation of two cobaloxime moieties might give useful information on the cis and trans influence in these systems. There has been much work [10,12–17,20] on the study of such effects by ^1H NMR in the mono-organocobaloximes.

The present paper reports the synthesis of organobridged dicobaloximes, $\text{Py}(\text{L})_2\text{Co}^{\text{III}}-(\text{CH}_2)_n-\text{Co}^{\text{III}}(\text{L})_2\text{Py}$, $\text{L} = \text{dmgH}^-$ and dpgH^- , $n = 3-6$ and 10] having varying length of alkyl chain between the two cobalt atoms. A preliminary account of the cis influence based on the ^1H NMR values is also reported.

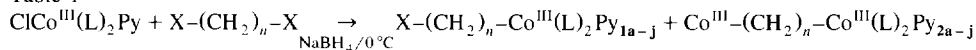
2. Results and discussion

In the reaction of Co^{I} with the dihalide, the best yield of the dicobaloximes is formed under the conditions (i) longer reaction time (overnight), (ii) using molar ratio of 1:2 or more for the dihalide: Co^{I} , and (iii) $\text{X} = \text{Br}$ or I ; condition (i) is the most crucial among all these (see Table 1). In general the second oxidative addition of Co^{I} to the dihalide that is path B (Scheme 1) is slower than the first one and is even slower for the dpgH^- complexes. The isolation of the intermediate haloalkylcobaloxime justifies this viewpoint. The prod-

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¹ gH^- = Glyoxime, dmgH^- = dimethylglyoxime, dpgH^- = diphenylglyoxime, mpgH^- = methylphenylglyoxime, chgH^- = cyclohexanedionedioxime (all mono anions).

Table 1



Product no. ^a	X-(CH ₂) _n -X		Reaction time/temp. (min/°C)	Dihalide:ClCo(III)	Yield (%) ^b	
	X	n			1	2
a	Br	3	300/0	1:2	trace	49
b	Br	4	13/0	1:2	20	3.4
b'	I	4	5/0	2:1	41	2
			720/25 ^c	1:2	1.6	86
c	Br	5	6/0	1:2	55	12
c'	Cl	5	150/0	1:2	15	4
d	Br	6	6/0	1:1	30	9
			720/25 ^c	1:2	4	88
e	Br	10	10/0	1:1	40	10
			720/0 ^c	1:2	trace	93
f	Br	3	8/0	2:1	16	4
			180/25	1:2	trace	25
g	Br	4	270/10 ^c	1:2	54	7.5
g'	I	4	6/0	2:1	15	9
			720/0 ^c	1:2	trace	20
h	Br	5	270/0	10:1	45	3.1
			720/0 ^{c,d}	1:2	4	11
h'	Cl	5	8/0	1:3.83	10	trace
			720/25	1:2.5	16	4
i	Br	6	300/0	1:2.5	9	8
j	Br	10	720/25	1:3.83	1	9

^a Product nos. **a–e** refer to dmgH complexes and **f–j** refer to dpgH complexes.

^b *R_f* values: dmgH complexes: (**1a–e**) 0.56–0.60 and (**2a–e**) 0.11–0.33 in ethyl acetate, dpgH complexes (**1f–j**) 0.30–0.40 and (**2f–j**) 0.06–0.12 in CCl₄:ethyl acetate (9:1), the dpgH complexes are less polar than the dmgH complexes. In general, all the dicobaloximes are stable at room temperature for months except **2a** and **2f** which decompose over a period of 1 month even when stored at 0°C.

^c Addition of the halide at 0°C and then the reaction mixture brought to RT and stirred.

^d The same reaction in acetonitrile gives 29% (mono) and 15% (di) after 13 min work-up and 40% (mono) and 16% (di) after 720 min.

ucts are characterized by the elemental analysis, ¹H NMR and FAB mass (see Tables 2–4).

The total yield of the dpgH cobaloximes is always lower than their dmgH analogues. This may be due to the weak nucleophilicity of the Co^I(dpgH)₂Py compared to the Co^I(dmgH)₂Py [21] and/or due to steric crowding by the bulky equatorial ligands. The X-ray crystallographic studies are under way to ascertain the orientation of the two cobaloxime moieties relative to each other.

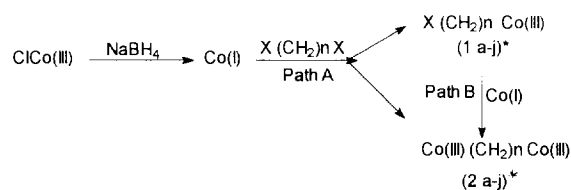
In general, the organocobaloximes are usually characterized by their ¹H NMR and elemental analyses. To the best of our knowledge there are no reports of mass spectral studies on such complexes. We have utilized FAB mass on four representative examples for more

information about these molecules (Table 4). In the haloalkylcobaloximes, the labile axial base pyridine is lost first followed by the cleavage of the Co–C bond and the loss of the haloalkyl group. Then the fragmentation of the cobaloxime core {Co(L)₂} begins. In the dicobaloximes, the two pyridine ligands are lost one after the other, followed by the cleavage of one Co–C bond with the loss of {Co(L)₂}.

The ¹H NMR spectra of the dicobaloximes are similar to the haloalkylcobaloximes, in general, but the latter have a characteristic triplet at around δ3.3 for the –CH₂ group.

Five sets of NMR values are considered: (i) the O–H ··· O; (ii) the cobalt-bound –CH₂; (iii) the rest of the alkyl chain; (iv) the equatorial ligand; (v) the Py (α and γ) resonances. In the dpgH complexes for the haloalkylcobaloximes as well as the dicobaloximes, the resonance for (i), (ii) and (v) appears at consistently lower field than the corresponding dmgH cobaloximes (see Fig. 1(a–e) and Fig. 2(a–d)). This, we believe, is due to the influence of the equatorial ligands [10,17]. The bar charts further indicate that: ²

(i) the magnitude of Δ_i (Δ_i = δ_i dpgH – dmgH,



Co = Co(dmgH)₂Py or Co(dpgH)₂Py

n = 4; X = I / Br

n = 5; X = Cl / Br

n = 6; X = Br

* = refer to table 1

Scheme 1.

² For uniformity, only X = Br is considered for comparison.

where δ_i (^1H NMR chemical shift) is larger in some cases than others;

(ii) for both the haloalkyl and the dicobaloximes, a plot of η (where $\eta = \text{av. } \Delta_i$) for the resonances ($\text{O}-\text{H} \cdots \text{O}$), $\text{Co}-\text{CH}_2$, P_α and P_γ shows that (Fig. 3(a))

$$\eta_{\text{O}-\text{H} \cdots \text{O}} \cong \eta_{\text{Co}-\text{CH}_2} > \eta_{\text{P}_\alpha} > \eta_{\text{P}_\gamma}$$

Δ_i , and hence η , (in general) can be considered to be the extent to which the resonances ($\text{OH} \cdots \text{O}$, $\text{Co}-\text{CH}_2$, P_α , P_γ) are influenced by substituting the methyl with the phenyl group in the equatorial ligand. It is also noteworthy that:

(i) for the $\text{O}-\text{H} \cdots \text{O}$ and the $\text{Co}-\text{CH}_2$ resonances (Fig. 3(a))

$$\eta(\text{dicobaloximes}) > \eta(\text{haloalkylcobaloximes})$$

(ii) for the P_α and the P_γ resonances (Fig. 3(a))

$$\eta(\text{dicobaloximes}) \cong \eta(\text{haloalkylcobaloximes})$$

(iii) for the $\text{X}-\text{CH}_2$ resonance, Δ_i decreases steadily with the length of alkyl chain and ultimately becomes negative for $n = 10$ (Fig. 3(b));

(iv) the $\text{O}-\text{H} \cdots \text{O}$ resonances for the dicobaloximes are always upfield than the haloalkyl cobaloxime (Fig. 3(c));

(v) no trend, if any, is perceptible in our data for the

P_α , P_γ $\text{dmgH}-\text{Me}$ and $\text{dpgH}-\text{Ph}$ resonances with increasing length of the alkyl chain for both the haloalkyl and the dicobaloximes.

3. Experimental

Chlorocobaloximes, $\text{ClCo}^{\text{III}}(\text{L}_2)\text{Py}$ $\text{L} = \text{dmgH}$, dpgH], 1,4-dibromobutane and 1,5-dibromopentane were synthesized by published procedures [15,22,23]. Diphenylglyoxime and all other dihalides were bought from Fluka AG. The ^1H NMR spectra were recorded on a Bruker WP-80 FT NMR spectrometer. The elemental analysis was carried out at the Regional Sophisticated Instrumentation Center (RSIC), Lucknow, and at IIT, Kanpur. FAB mass was done at RSIC, Lucknow.

The dicobaloximes have been synthesized by the reaction of $\text{Co}^{\text{I}}(\text{L})_2\text{Py}$ with the corresponding dihalide under strict anaerobic conditions at 0°C (Scheme 1). The work-up procedure is similar to the organocobaloximes as detailed earlier [15,24]. It was observed that in certain cases the precipitation of the cobaloxime did not occur on pouring the reaction mixture into water, instead an orange-red emulsion formed. In those cases the emulsion was extracted with

Table 2
 ^1H NMR chemical shifts δ (ppm, CDCl_3) for **1a–j** to **2a–j**

Compound no.	$\text{O}-\text{H} \cdots \text{O}$ (s) ^a	P_α (d) [$J = 5 \text{ Hz}$]	P_γ (m)	P_δ (m)	L^b	$\text{X}-(\text{CH}_2)_n-$ (t) ^c [$J = 6.25 \text{ Hz}$]	$\text{Co}-(\text{CH}_2)$ (m)	$-(\text{CH}_2)_{n-2}-$ (m)
1a	18.09	8.56	7.65	7.28	2.13	3.19	— ^d	1.00–1.56
2a	18.06	8.52	7.61	7.29	2.14	—	— ^d	1.23–1.62
1b	18.22	8.56	7.66	7.31	2.11	3.34	1.68	0.68–1.96
2b	18.06	8.52	7.62	7.25	2.10	—	1.56	0.50–1.06
1b'	18.39	8.56	7.64	7.28	2.15	3.12	1.64	0.04–1.31
1c	18.22	8.5	7.62	7.25	2.12	3.31	1.68	0.62–1.53
2c	18.06	8.56	7.62	7.28	2.17	—	1.56	0.50–1.25
1c'	18.46	8.50	7.56	7.21	2.12	3.37	1.54	0.59–1.37
1d	18.20	8.5	7.59	7.21	2.12	3.31	1.57	0.64–1.40
2d	18.06	8.56	7.59	7.21	2.12	—	1.56	0.43–1.31
1e	18.39	8.50	7.59	7.18	2.11	3.34	— ^d	0.37–1.34
2e	18.41	8.56	7.62	7.28	2.11	—	1.59	0.37–1.43
1f	18.65	8.84	7.71	— ^d	7.19	3.37	2.00	1.62–1.06
2f	18.99	8.92	7.74	— ^d	7.13	—	2.13	0.92–1.82
1g	18.78	8.93	7.84	— ^d	7.25	3.46	2.18	1.31–2.00
2g	18.60	8.93	7.75	— ^d	7.18	—	2.31	0.62–1.87
1g'	18.66	8.90	7.76	— ^d	7.28	3.21	2.18	1.06–1.93
1h	18.75	8.93	7.81	— ^d	7.25	3.39	2.18	0.56–2.00
2h	18.86	8.93	7.76	— ^d	7.11	—	2.25	1.00–1.81
1h'	18.56	8.87	7.71	— ^d	7.20	3.46	2.12	0.93–1.93
1i	18.69	8.92	7.78	— ^d	7.20	3.37	2.18	0.62–2.00
2i	18.65	8.92	7.72	— ^d	7.15	—	2.25	1.93–1.06
1j	18.59	8.90	7.71	— ^d	7.20	3.31	2.15	0.62–1.93
2j	18.60	8.93	7.78	— ^d	7.18	—	2.25	0.75–1.81

^a Broad **1** and **2** (a–e), sharp **1** and **2** (f–j).

^b Singlet **1** and **2** (a–e), multiplet **1** and **2** (f–j).

^c Triplet or merged with the alkyl chain.

^d Resonances merge and/or integrate together.

dichloromethane, the solvent layer was washed several times with brine, dried over anhydrous sodium sulphate and the volume concentrated to a few millilitres. The precipitation was then achieved by pouring it dropwise into light petroleum with constant stirring. The solid was filtered and then dried in vacuum.

In each reaction a mixture of haloalkylcobaloxime (**1**) and the dicobaloxime (**2**) was obtained. The ratio of

the two was found to depend on the reaction time, temperature, and the molar ratios of the chlorocobaloxime and the dihalide (see Table 1). The separation of the two products posed a lot of problems. Various adsorbents (silica gel and basic alumina), solvent systems (carbon tetrachloride–ethylacetate, pet.ether–chloroform–ethylacetate), column dimensions and flash chromatography were tried. The separation

Table 3
Elemental analysis and R_f values for compounds **1a–j** to **2a–j**

Compound nos.	R_f ^a	Anal. Calcd. for	Found (calculated) (%)			
			C	H	N	Br/Cl/I
1a	0.56	CoC ₁₇ H ₂₅ N ₅ O ₄ Br	39.28 (39.17)	5.18 (5.14)	14.26 (14.29)	16.37 (16.30)
2a	0.16	Co ₂ C ₂₉ H ₄₄ N ₁₀ O ₈	44.73 (44.71)	5.68 (5.65)	18.02 (17.99)	
1b	0.58	CoC ₁₆ H ₂₅ N ₅ O ₄ Br	40.49 (40.46)	5.37 (5.39)	13.92 (13.89)	15.88 (15.85)
2b	0.12	Co ₂ C ₃₀ H ₄₆ N ₁₀ O ₈	45.41 (45.43)	5.90 (5.85)	17.61 (17.67)	
1b'	0.60	CoC ₁₇ H ₂₇ N ₅ O ₄ I	36.99 (37.01)	4.91 (4.93)	12.88 (12.70)	23.10 (23.05)
1c	0.58	CoC ₁₈ H ₂₉ N ₅ O ₄ Br	41.63 (41.69)	5.601 (5.64)	3.581 (3.51)	14.48 (14.42)
2c	0.15	Co ₂ C ₃₁ H ₄ N ₁₀ O ₈	46.19 (46.13)	5.91 (6.00)	17.30 (17.37)	
1c'	0.62	CoC ₁₈ H ₂₉ N ₅ O ₄ Cl	46.00 (45.60)	6.211 (6.17)	5.01 (4.78)	7.45 (7.48)
1d	0.60	CoC ₁₉ H ₃₁ N ₅ O ₄ Br	43.02 (42.84)	5.82 (5.87)	13.21 (13.16)	14.90 (15.01)
2d	0.12	Co ₂ C ₃₂ H ₅₀ N ₁₀ O ₈	46.76 (46.81)	6.11 (6.14)	17.11 (17.07)	
1e	0.56	CoC ₂₃ H ₃₉ N ₅ O ₄ Br	47.00 (46.92)	6.63 (6.08)	11.93 (11.90)	13.56 (13.58)
2e	0.12	Co ₂ C ₃₆ H ₅₈ N ₁₀ O ₈	49.25 (49.29)	6.71 (6.67)	16.01 (15.98)	
1f	0.31	CoC ₃₆ H ₃₃ N ₅ O ₄ Br	58.57 (58.52)	4.48 (4.50)	9.50 (9.48)	10.87 (10.82)
2f	0.12	Co ₂ C ₆₉ H ₆₀ N ₁₀ O ₈	65.01 (64.97)	4.73 (4.74)	10.97 (10.99)	
1g	0.45	CoC ₃₇ H ₃₅ N ₅ O ₄ Br	58.99 (59.03)	4.66 (4.69)	9.32 (9.31)	10.65 (10.62)
2g	0.09	Co ₂ C ₇₀ H ₆₂ N ₁₀ O ₈	65.21 (65.19)	4.84 (4.85)	10.90 (10.87)	
1g'	0.47	CoC ₃₇ H ₃₅ N ₅ O ₄ I	55.59 (55.55)	3.39 (4.41)	8.78 (8.76)	15.85 (15.87)
1h	0.38	CoC ₃₈ H ₃₇ N ₅ O ₄ Br	59.55 (59.51)	4.87 (4.86)	8.33 (8.35)	10.44 (10.42)
2h	0.07	Co ₂ C ₇₁ H ₆₄ N ₁₀ O ₈	65.42 (65.41)	5.00 (4.95)	10.72 (10.75)	
1h'	0.29	CoC ₃₈ H ₃₇ N ₅ O ₄ Cl	63.20 (63.18)	5.12 (5.16)	9.68 (9.70)	4.89 (4.91)
1i	0.30	CoC ₃₉ H ₃₉ N ₅ O ₄ Br	60.00 (59.98)	5.09 (5.03)	8.95 (8.97)	10.25 (10.2)
2i	0.08	Co ₂ C ₇₂ H ₆₆ N ₁₀ O ₈	65.66 (65.63)	5.07 (5.05)	10.64 (10.63)	
1j	0.38	CoC ₄₃ H ₄₇ N ₅ O ₄ Br	61.73 (61.70)	5.68 (5.66)	8.39 (8.37)	9.54 (9.55)
2j	0.46	Co ₂ C ₇₆ H ₇₄ N ₁₀ O ₈	66.47 (66.44)	5.43 (5.44)	10.17 (10.20)	

^a **1** and **2** (a–e) in EtOAc, **1** and **2** (f–j) in CCl₄:EtOAc 9:1.

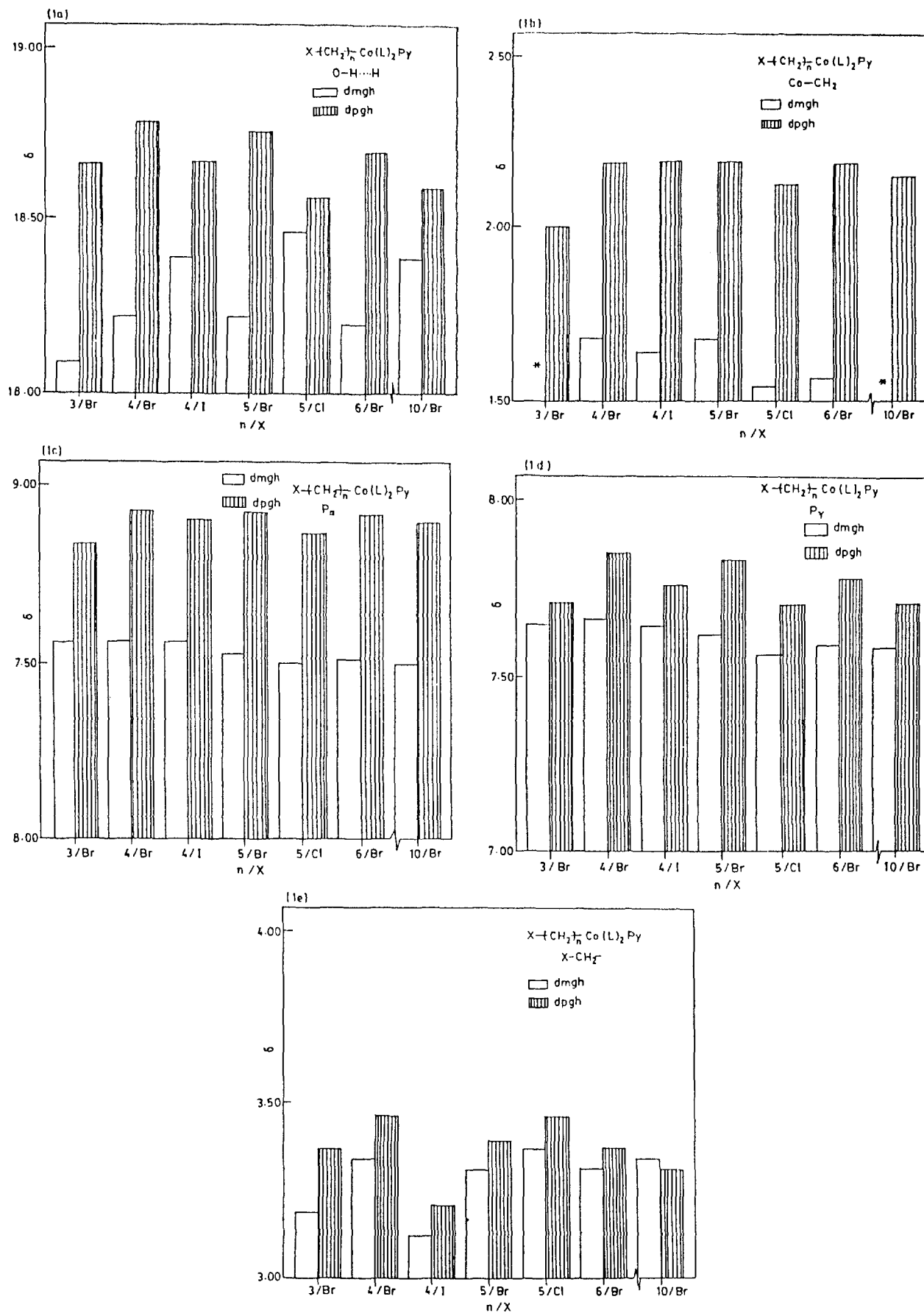


Fig. 1. NMR data. * indicates resonances not resolved.

could be achieved by any of the following procedures, however the procedure (i) was found to be the best.

3.1. dmgh complexes

(i) The orange-red powder containing the mixture of cobaloxime was separated by silica gel (100–200 mesh) using chloroform–ethylacetate mixture. The column was pre-eluted with chloroform and then the polarity was increased with ethylacetate (10–40%) until two distinct bands were visible. The first red band corresponding to the haloalkylcobaloxime separated out completely with ethylacetate–chloroform mixture. The solvent system was then gradually changed to ethylacetate–methanol (80–20) when the second red band corresponding to the dicobaloxime separated.

Table 4

FAB mass spectral data

Compound no.	Principal peaks (relative intensity) ^a
1b	M 505 (35), M + 1 506 (25), 426 (90), 289 (100), 80 (24)
2c	728 (15), 649 (44), 359 (50), 289 (100), 80 (15)
2h	1124 (5), 1145 (12), 607 (30), 538 (100), 537 (75)
1h'	M 721 (15), M + 1 722 (14), 643 (40), 642 (29), 538 (100), 537 (100)

^a See text for detail.

(ii) The mixture of cobaloximes dissolved in minimum volume of chloroform was adsorbed on basic alumina (Brockman grade 1). The dried powder was

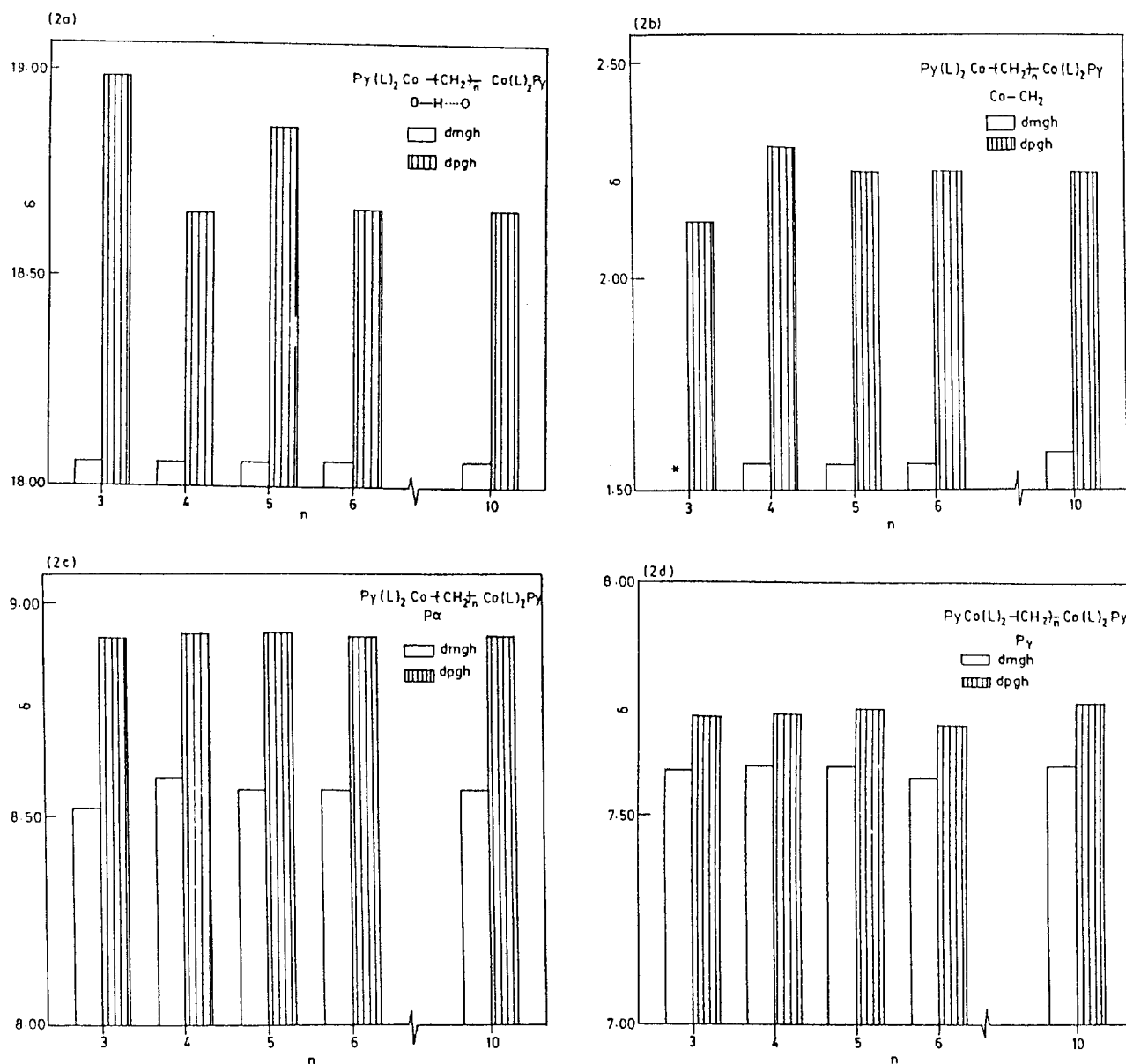


Fig. 2. NMR data. * indicates resonances not resolved.

then loaded on a basic alumina column pre-eluted with pet.ether. The polarity of the eluent was increased with chloroform (10–20%); the haloalkylcobaloxime eluted out first as a red band. The dicobaloxime came out neatly with chloroform–pet.ether (40–60) mixture.

(iii) The mixture of cobaloximes, dissolved in minimum volume of chloroform, was adsorbed on silica gel (TLC grade). This was then loaded on a silica gel column pre-eluted with chloroform. The elution was done very carefully with chloroform, chloroform–ethylacetate, ethylacetate–methanol mixture until two distinct bands separated one after the other. The flow of solvent was maintained by suction using an aspirator. The entire process had to be done slowly to achieve a neat separation.

3.2. *dpgH* complexes

The best separation was achieved by loading the mixture on silica gel column (100–200 mesh) using chloroform. The polarity of the solvent was increased with ethylacetate (2–4%) till three distinct bands were visible. The first band corresponding to the haloalkylcobaloxime came out followed by a pale yellow-brown band corresponding to the unreacted chlorocobaloxime. The dicobaloxime eluted out only with 5–6% ethylacetate mixture. It is important to note that any further increase in polarity at this stage contaminates the dicobaloxime with cobaloxime(II) impurity which elutes out at the same time. Any such contamination hampers the NMR study.

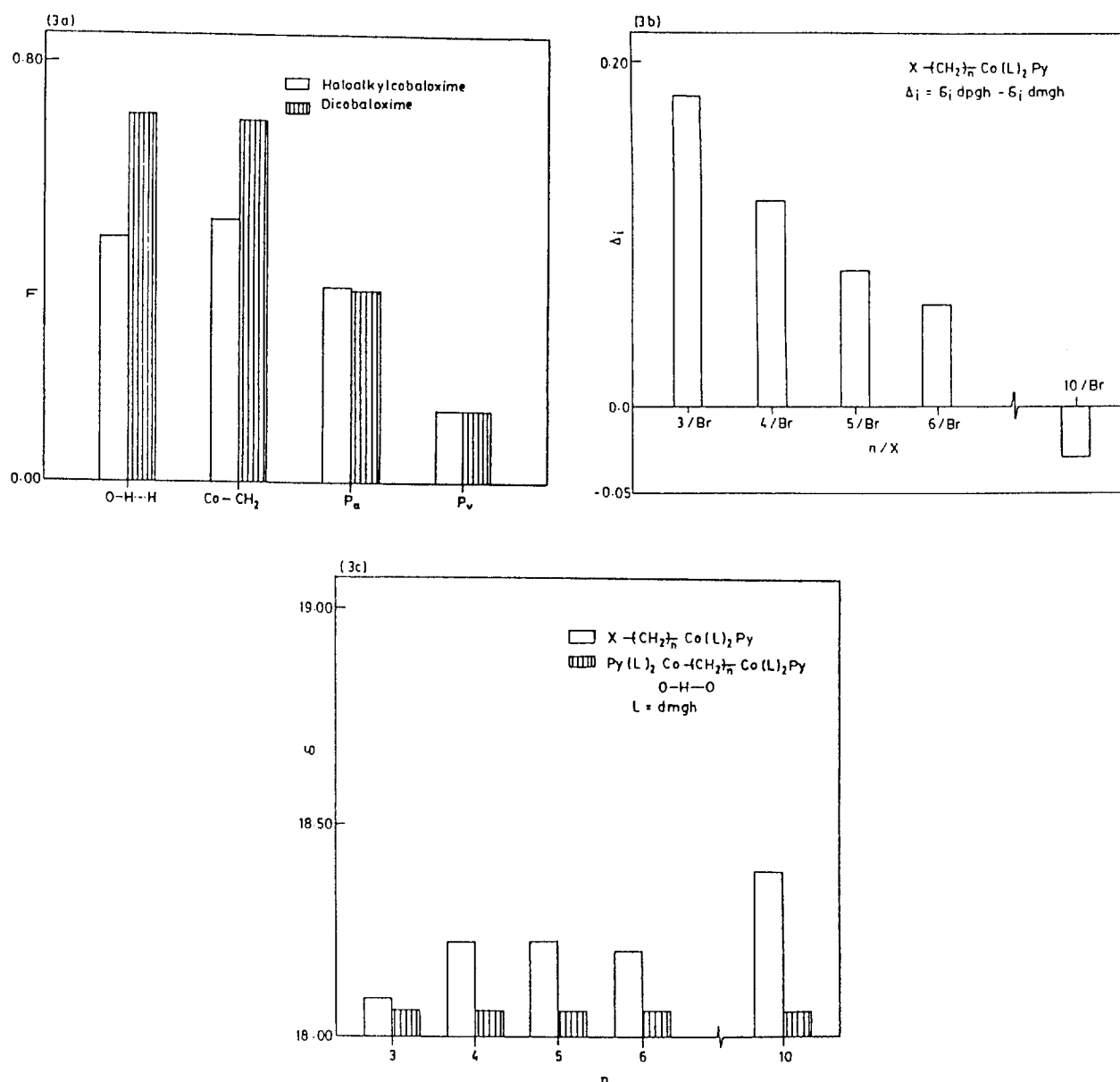


Fig. 3.

3.3. Synthesis of organobridged dicobaloxime from haloalkylcobaloxime

(i) The haloalkylcobaloxime (**1d**, 1 mmol) was reacted with cobaloxime(I) (2 mmol) under strict anaerobic conditions at 0°C in aqueous methanol (path B, Scheme 1). Though the reaction was visibly over within 15 min with distinct change in colour from blue to red, the mixture was left stirring overnight at room temperature. The product was isolated by pouring the reaction mixture into water containing a few drops of pyridine. The separation by column is the same as described above. Yield 95%.

(ii) Following a similar procedure, the dpGH cobaloximes gave only 10–20% yield at most. However, change of solvent to aqueous acetonitrile improved the yield to 65%. Solubility may be one reason as the haloalkylcobaloxime is only partially soluble in aqueous methanol.

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References

- [1] (a) G.N. Schrauzer, *Acc. Chem. Res.*, **1** (1968) 97 and references cited therein. (b) L. Randaccio, S. Geremia, E. Zangrando and C. Ebert, *Inorg. Chem.*, **33** (1994) 4641. (c) P.J. Toscano, E. Barren, H. Brand, L. Konieczny, E.J. Schermerborn, K. Shufen and S. vanWinkler, ACS Symp. Ser., Vol. 286, *Inorganic Fluorine Chemistry*, 1994, p. 555. (d) Y. Ohashi and H. Uekusa, *Kagaku (Kyoto)*, **50** (1995) 126.
- [2] N. Bresciani-Pahor, M. Forcolin, L.G. Marzilli, L. Randaccio, M.F. Summers and P.J. Toscano, *Coord. Chem. Rev.*, **63** (1985) 1 and references cited therein.
- [3] L. Randaccio, N. Bresciani-Pahor, E. Zangrando and L.G. Marzilli, *Chem. Rev.*, (1989) 225 and references cited therein.
- [4] E.J. Starr, S.A. Broune, M.R. Caria and J.R. Moss, *J. Organomet. Chem.*, **490** (1995) C-20.
- [5] G.N. Schrauzer, L.P. Lee and J.W. Sibert, *J. Am. Chem. Soc.*, **92** (1970) 2997.
- [6] (a) D. Dolphin (Ed.), *Vit B12*, Vols. 1 & 2 Wiley-Interscience, New York, 1982. (b) J. Halpern, *Science*, **227** (1985) 869.
- [7] (a) A.K. Ghosh and Y. Chen, *Tetrahedron Lett.*, **36** (1995) 505. (b) S. Sukamoio, Y. Kondo and S. Igarashi, *Heterocycles*, **41** (1995) 1771. (c) Y. Takahashi, Y. Honda and T. Tsuchya, *Carbohydr. Res.*, **270** (1995) 77. (d) B.P. Brauchaud and R.M. Slade, *Tetrahedron Lett.*, **35** (1994) 4071. (e) M. Kijima, K. Nakazato and T. Sato, *Chem. Lett.*, **2** (1994) 347. (f) B.P. Brauchaud, R.M. Siade and S.K. Janisse, *Tetrahedron Lett.*, **34** (1993) 7885. (g) L.I. Simandi, T.M. Barna, L. Koreeze and A. Rockenbauer, *Tetrahedron Lett.*, **34** (1993) 317.
- [8] (a) J. Hartung, B. Hertel and F. Trach, *Chem. Ber.*, **126** (1993) 1187. (b) M.R. Domingo, A. Irving, Y.H. Liao, J.R. Moss and A. Nash, *J. Organomet. Chem.*, **443** (1993) 233. (c) B. Fraser, L. Braund, W.K. Stoval, H.D. Kaesz, S.I. Khan and F. Maury, *J. Organomet. Chem.*, **472** (1994) 317. (d) V.I. Tsapkov, N.N. Samus and M.V. Gandzii, *Zh. Neorg. Khim.*, **39** (1994) 252. (e) M.D. Mazus, Y.A. Simpnov, L. Parata, M. Nayagoyu, K. Turte and V.N. Shafranskii, *Koord. Khim.*, **20** (1994) 376. (f) W.M. Wright, T. Smalley, M.E. Welker, Jr., A. Rheingold and L. Arnold, *J. Am. Chem. Soc.*, **116** (1994) 6777.
- [9] B.D. Gupta and S. Roy, *Inorg. Chim. Acta*, **96** (1985) 193.
- [10] P.J. Toscano, T.I. Swilder and L.G. Marzilli, *Inorg. Chem.*, **22** (1983) 3416.
- [11] (a) N. Bresciani-Pahor, L. Randaccio, E. Zangrando and P.J. Toscano, *Inorg. Chim. Acta*, **96** (1985) 193. (b) B.D. Gupta and S. Roy, *Inorg. Chim. Acta*, **146** (1988) 209. (c) A. Uchida, Y. Ohashi, Y. Sasada, and Y. Ohgo, *Acta Crystallogr. Sect. C*, **41** (1985) 25. (d) D. Dodd, M.D. Johnson and B.L. Lockman, *J. Am. Chem. Soc.*, **99** (1977) 3664. (e) C.J. Cooksey, D. Dodd, M.D. Johnson and B.L. Lockman, *J. Chem. Soc. Dalton Trans.*, (1978) 1814. (f) A. Misono, Y. Uchida, M. Hidai and H. Kanai, *Bull. Chem. Soc. Jpn.*, **40** (1967) 2087. (g) V.I. Borodulina-Shivets, I. Rudakova and A.V. Ablov, *Zh. Obshch. Khim.*, **40** (1970) 703 (*J. Gen. Chem. USSR*, **40** (1970) 676). (h) N.M. Samus, O.N. Damasquina and A.V. Ablov, *Zh. Neorg. Khim.*, **18** (1973) 229 (*Russ. J. Inorg. Chem., Engl. Transl.* **18** (1973) 229).
- [12] C. Lopez, S. Alvarez, X. Solans, and M. Font-Altaba, *Inorg. Chim. Acta*, **121** (1986) 71.
- [13] C. Lopez, S. Alvarez, X. Solans and M. Font-Altaba, *Inorg. Chem.*, **25** (1986) 2962.
- [14] C. Lopez, S. Alvarez, X. Solans and M. Font-Altaba, *Inorg. Chim. Acta*, **133** (1987) 101.
- [15] C. Lopez, S. Alvarez, M. Font-Bardia and X. Solans, *J. Organomet. Chem.*, **414** (1991) 245 and references cited therein.
- [16] C. Lopez, S. Alvarez, M. Aguilo, X. Solans and M. Font-Altaba, *Inorg. Chim. Acta*, **127** (1987) 153.
- [17] J.M. Gilaberte, C. Lopez, S. Alvarez, M. Font-Bardia and X. Solans, *New J. Chem.*, **17** (1993) 193 and references cited therein.
- [18] G.N. Schrauzer and R.J. Windgassen, *J. Am. Chem. Soc.*, **88** (1966) 3738.
- [19] S.N. Anderson, D.H. Ballard and M.D. Johnson, *J. Chem. Soc. Perkin Trans. 2*, (1972) 311.
- [20] (a) H.A.O. Hill and K.J. Moralee, *J. Chem. Soc. A*, (1969) 554. (b) W.C. Trogler, R.C. Stewart, L.A. Epps and L.G. Marzilli, *Inorg. Chem.*, **13** (1974) 1564. (c) W.C. Trogler and L.G. Marzilli, *Inorg. Chem.*, **14** (1975) 2942. (d) P.L. Gauss and A.L. Crumbliss, *Inorg. Chem.*, **15** (1976) 2082. (e) N. Bresciani-Pahor, L. Randaccio and P.J. Toscano, *J. Chem. Soc. Dalton Trans.*, (1982) 1559. (f) L.G. Marzilli, P. Politzer, W.C. Trogler and R.C. Stewart, *Inorg. Chem.*, **14** (1975) 2389 and references cited therein. (g) C. Bied-Chareton, A. Gaudemer, C.A. Chapman, D. Dodd, B.D. Gupta, M.D. Johnson, B.L. Lockman and B. Septe, *J. Chem. Soc. Dalton Trans.*, (1978) 1807.
- [21] G.N. Schrauzer and E. Deutsch, *J. Am. Chem. Soc.*, **91** (1969) 3341.
- [22] G.N. Schrauzer, *Inorg. Synth.*, **11** (1968) 61.
- [23] A.I. Vogel, *A Text Book of Practical Organic Chemistry Including Qualitative Organic Analysis*, ELBS, 1968, p. 283.
- [24] E. Zangrado, N. Bresciani-Pahor, L. Randaccio, J.P. Charland and L.G. Marzilli, *Organometallics*, **5** (1986) 1938.