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Preparation and reactivity with isocyanide of bromomalonaldehyde complexes of iron, cobalt, nickel, and copper

Gabriele Albertin *, Daniela Baldan, and Emilio Bordignon *

Dipartimento di Chimica dell'Università di Venezia, 30123 Venice (Italy)

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Abstract

The reactions of bromomalonaldehyde anion (BMA) with several metal(II) chlorides have been studied and the syntheses of the tris(chelate) $AsPh_4[Fe(BMA)_3]$ complex and the complexes $[M(BMA)_2(H_2O)_2]$ and $[M(BMA)_2]$ ($M = Fe^{II}$, Co^{II}, Ni^{II}, Cu^{II}) are reported. Complexes $CoBr_2(CNR)_4$, $[FeBr(CNR)_5]BPh_4$ and $[Cu(CNR)_4]Br$ ($R = 4\text{-}CH_3C_6H_4$) were obtained by reaction of the BMA derivatives with RNC.

Introduction

Although many studies on the synthesis, structure, molecular association, and reactivity of β-dicarbonyl complexes have been reported [1] there have been few studies concerned with the chelating properties of dialdehydes [2], which may be regarded as the simplest 1,3-dicarbonyl ligands. We previously reported the reaction of the nitromalonaldehyde (NMA) with several metal(II) chlorides, which allowed synthesis of the first examples of monomeric tris(chelate) $[M(NMA)_3]^-$ ($M = Co^{II}$ and Fe^{II}) complexes [3]. This result was tentatively explained in terms not only of the low steric hindrance of the dialdehyde ligand as compared with variously substituted acetylacetonates but also of the presence of an electron-withdrawing group (NO_2) on the ligand. In order to confirm this suggestion, we studied the reactions of metal(II) chlorides with bromomalonaldehyde, which has steric requirements very similar to those of nitromalonaldehyde but different electronic properties resulting from replacement of the NO_2 group by bromine. We describe here the results of these studies on the chelating properties of bromomalonaldehyde, which have led to the synthesis of new bis(chelate) and tris(chelate) complexes. The reactions of these chelate complexes with arylisocyanides have been examined, and the results compared with those previously obtained with the nitromalonaldehyde complexes.

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Results and discussion

The bromomalonaldehyde anion (BMA) reacts in aqueous solution with metal(II) chlorides in the molar ratio 2/1 to give $[M(BMA)_2(H_2O)_2]$ ($M = Fe^{II}$, Co^{II}, Ni^{II}) and $Cu(BMA)_2$ compounds, which have been isolated and characterized. The corresponding $[M(BMA)_2]$ complexes may be obtained by heating the aquo complexes at 50 °C under high vacuum.

Selected properties of the complexes are reported in Table 1. Unfortunately the bis(chelate) compounds are insoluble in polar and non-polar solvents and therefore characterization in solution, and the gaining of information on the presence in solution of monomeric or polymeric species, by electronic spectroscopy and molecular weight measurements, is not possible.

The IR spectra for the BMA complexes show a strong-band at 1662–1590 cm^{-1} attributed to the $\nu(CO)$ of the coordinated dialdehyde. This band appears at 1630 cm^{-1} for the free ligand $Na[C_3H_2O_2Br]$.

The magnetic moments of the $[M(BMA)_2]$ complexes in the solid state at 25 °C, which are 5.31 and 4.98 μ_B for iron(II) and cobalt(II) compounds respectively, are characteristic of octahedral species and similar to those reported for the corresponding acetylacetonate derivatives [4,5]. Furthermore, the reflectance spectrum of $[Fe(BMA)_2]$ is very similar to that of the octahedral $AsPh_4[Fe(BMA)_3]$ complex, and the spectrum of $[Co(BMA)_2]$ found to be closely similar to the spectra of $[Co(acac)_2]_4$ and $[Co(NMA)_2]$ derivatives [5,6,3]. It is thus suggested that the bromomalonaldehyde complexes, like the acetylacetonate complexes, are polymeric, with bridging oxygen atoms forming an octahedral environment for the central metal. The bis(chelate) $[M(BMA)_2]$ complexes were shown to form adducts with

Table 1

Selected properties of bromomalonaldehyde complexes.

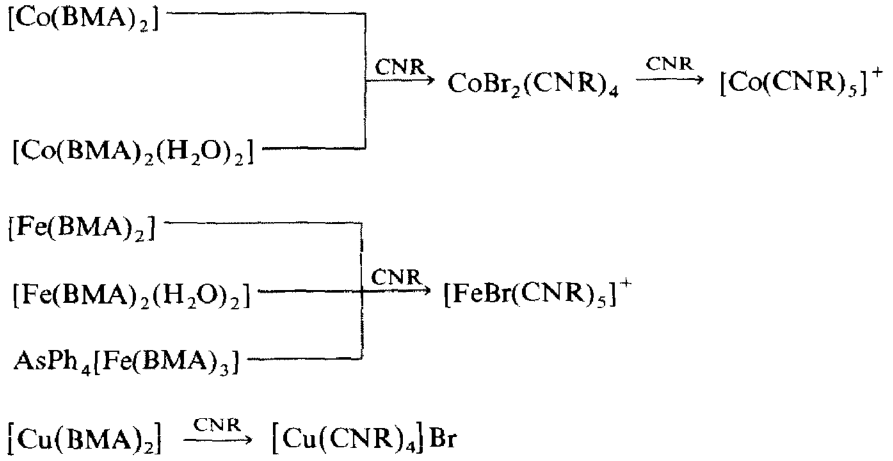
Compounds	IR [a] (cm^{-1})		μ eff. [d]	Electronic spectra	
	$\nu(CO)$ [b]	$\nu(CN)$	μ_B	Medium	λ_{max} (nm)
$[Fe(BMA)_2]$	1612		5.31	Nujol	480
$[Fe(BMA)_2(H_2O)_2]$	1660		5.36	Nujol	476
$AsPh_4[Fe(BMA)_3]$	1650		5.24	CH_2Cl_2	408sh 482 [e]
				Nujol	485
$[Co(BMA)_2]$	1612		4.92	Nujol	470sh 510
$[Co(BMA)_2(H_2O)_2]$	1662		4.98	Nujol	472 504
$[Co(BMA)_2Py_2]$	1626		4.95	Nujol	472 500 540sh
$[Ni(BMA)_2(H_2O)_2]$	1662		3.21	Nujol	648 720sh
$[Ni(BMA)_2Py_2]$	1626		3.19	Nujol	585
$[Cu(BMA)_2]$	1590		1.84	Nujol	644
$[FeBr(4\text{-}CH_3C_6H_4NC)_5]BPh_4$		2210w2160s (2214w2170s) [c]	diamag.	–	–
$CoBr_2(4\text{-}CH_3C_6H_4NC)_4$		2190s (2184s) [c]	2.19	–	–
$[Cu(4\text{-}CH_3C_6H_4NC)_4]Br$		2160s (2152s2168sh) [c]	diamag.	–	–

[a] In KBr pellets. [b] $\nu(CO)$ $Na(C_3H_2O_2Br)$ at 1630 cm^{-1}. [c] In CH_2Cl_2 solution. [d] In the solid state at 25 °C. [e] $\in$ 4900 dm^3 mol^{-1} cm^{-1}.

neutral donor molecules such as H_2O and pyridine, to give six-coordinate complexes which were isolated and characterized (Table 1).

In the presence of an excess of bromomalonaldehyde, the reaction with metal(II) chloride proceeds to give monomeric tris(chelate) $[M(BMA)_3]^-$ complexes, isolated as BPh_4 salts, only in the case of iron(II), the bis(chelate) derivatives being exclusively obtained with Co^{II}, Ni^{II}, and Cu^{II}. The $[Fe(BMA)_3]^-$ compound is a 1/1 electrolyte, stable as a solid and in solutions of polar solvents. The magnetic moment of 5.24 μ_B is consistent with a high-spin configuration. Comparison of our results with those previously obtained with variously substituted acetylacetonates [4–7] and nitromalonaldehyde [3] confirms the observation that the formation of monomeric tris(chelate) complexes can be obtained with a β-dicarbonyl ligand of low steric hindrance containing a good electron-withdrawing group, which lowers the basicity of the coordinated oxygen atoms. Bis(acetylacetonate) complexes of cobalt(II) and iron(II) are polymeric [4,6,7], and the first tris(chelate) complexes reported were with nitromalonaldehyde [3]. Replacement of the nitro group of NMA by the more weakly electron-withdrawing bromine atom gives a tris(chelate) complex with Fe^{II} $[Fe(BMA)_3]^-$, and only bis(chelate) complexes with cobalt(II) and nickel(II). Since the steric properties of NMA and BMA are comparable, the tendency to form tris(chelate) M^{II} complexes rather than polymeric bis(chelate) M^{II} complexes must be attributed to electronic rather than steric factors. The electron-withdrawing power of the nitro and bromo groups lowers the donor tendency of the β-dicarbonyl oxygen atoms, so that these ligands chelate a single metal atom rather than bridging two or more metal atoms. The electron-withdrawing hexafluoro acetylacetonate ligand (hfac) also gave a tris complex with cobalt(II).

We studied the reaction of the bromomalonaldehyde complexes with the isocyanide $4\text{-}CH_3C_6H_4NC$ (CNR) *. The results are summarized in Scheme 1.



Interestingly, both cobalt compounds $[Co(BMA)_2]$ and $[Co(BMA)_2(H_2O)_2]$ react with an excess of the isocyanide in boiling acetone to give the green paramagnetic $CoBr_2(CNR)_4$ complex, which reacts further with the isocyanide to give the

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* The isocyanides C_6H_5NC and $4\text{-}CH_3OC_6H_4NC$ gave similar results.

cobalt(I) $[Co(CNR)_5]^+$ derivative [8]. The formation of the $[CoBr_2(CNR)_4]$ compound is rather unexpected, since the bromide ligand must come from the bromomalonaldehyde of the starting complex.

The reaction of the previously-reported nitromalonaldehyde complexes $[Co(NMA)_2]$ and $[Co(NMA)_2(H_2O)_3]$ with isocyanide gave the $[Co(CNR)_5]$ $[Co(NMA)_3]$ derivative [3] and, similarly, the hexafluoroacetylacetonate (hfac) complex $[Co(hfac)_2]$ gave the $[Co(CNR)_5][Co(hfac)_3]$ derivative [3] in the reaction with isocyanide. In the present study with $[Co(BMA)_2]$ and $[Co(BMA)_2(H_2O)_2]$, no evidence of the formation of tris(chelate) complexes was observed. The reduction to cobalt(I) requires the further addition of CNR to give the $[Co(CNR)_5]^+$ derivative. The different behaviour of BMA compared to NMA and hfac ligands is thus shown by the reactions of the bis(chelate)-cobalt(II) with isocyanides. The reactions of the cobalt(II) complexes with the more strongly electron-withdrawing ligands form the tris(chelate) complexes $[Co(NMA)_3]^-$ and $[Co(hfac)_3]^-$ anions, but the NMA complex is reduced fully to $[Co(RNC)_5]^+$.

The reaction of iron bromomalonaldehyde chelates with isocyanide gives the $[FeBr(CNR)_5]^+$ cation, whereas $[Cu(BMA)_2]$ is reduced to form the tetrakis(isocyanide)copper(I) derivative [9]. Some properties of the isocyanide complexes are shown in Table 1. The IR spectrum of $CoBr_2(CNR)_4$ in the $\nu(CN)$ region shows only one strong band both in the solid state and in CH_2Cl_2 solution, attributed to the e_u-mode of the *trans*-$CoBr_2(CNR)_4$ complex. The magnetic moment of 2.19 μ_B is as expected for an octahedral low-spin cobalt(II) complex.

The IR spectrum of the $[FeBr(CNR)_5]^+$ derivative previously made in a different way [10] has a strong band at 2170 cm^{-1} and weak absorption at 2214 cm^{-1}. On the other hand, while only one band is observed in the solid state, two $\nu(CN)$ bands are present in the solution spectrum of $[Cu(CNR)_4]Br$ compound. This is attributed to the formation of $[Cu(CNR)_3]^+$ or $[Cu(CNR)_2]^+$ species [9].

Experimental

General consideration. All solvents used were purified and dried by standard methods. Sodium bromomalonaldehyde Na(BMA) was prepared by Trofimenko's method [11]. 4-Tolyl isocyanide was made as described in ref. 12. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin–Elmer model 683. Solid state spectra were obtained with potassium bromide pellets, while dichloromethane solution spectra were obtained with KBr solution cells (path length 0.5 mm). Proton magnetic resonance spectra were recorded on a Varian FT-80A instrument with tetramethylsilane as internal standard. Electronic spectra at room temperature were recorded on a Cary 219 spectrometer. Magnetic susceptibility measurements were performed on powdered samples at room temperature with a Cahn Instrument Faraday balance, with $Hg[Co(NCS)_4]$ as standard. Susceptibilities were corrected for diamagnetism of ligands from tables given by Figgis and Lewis [13]. Conductivities of 10^{-3} *M* solutions of the complexes in nitromethane at 25 °C were measured with a "Halosis" bridge.

Synthesis of complexes

$[M(BMA)_2(H_2O)_2]$ ($M = Fe^{II}$, Co^{II}, Ni^{II}) and $[Cu(BMA)_2]$. A slight excess (2.1 g, 12 mmol) of $Na(C_3H_2O_2Br)$ in 10 ml of water was added to an aqueous solution

(5 ml) of metal(II) chloride (5 mmol) at room temperature. The mixture was vigorously stirred until a solid separated. The product was filtered off and dried under vacuum. Further amounts of the solid could be obtained by slow evaporation of the mother liquor; yield $\geq$ 60%. The complexes were not recrystallized owing to their low solubility in polar and non-polar solvents. Anal. Found: C, 18.35; H, 1.87. $C_6H_8Br_2FeO_6$ calcd.: C, 18.39; H, 2.06%. Found: C, 18.10; H, 1.96. $C_6H_8Br_2CoO_6$ calcd.: C, 18.25; H, 2.04%. Found: C, 18.06; H, 1.84. $C_6H_8Br_2NiO_6$ calcd.: C, 18.26; H, 2.04%. Found: C, 20.05; H, 1.15. $C_6H_4Br_2CuO_4$ calcd.: C, 19.83; H, 1.11% m.p. 139 °C.

[M(BMA)$_2$] (M = Fe^{II} and Co^{II}). The bis(bromomalonaldehyde) complexes were obtained from the corresponding water adducts by heating at 45–50 °C under high vacuum (ca. 10^{-8} atm) for 8–10 h. However, in the case of the nickel complex, an impure material was always obtained. Anal. Found: C, 20.14; H, 1.15. $C_6H_4Br_2FeO_4$ calcd.: C, 20.26; H, 1.13%; m.p. > 250 °C. Found: C, 19.94; H, 1.04. $C_6H_4Br_2CoO_4$ calcd.: C, 20.08; H, 1.12%; m.p. > 250 °C.

[M(BMA)$_2$Py$_2$] (M = Co^{II} and Ni^{II}). A large excess of pyridine was added to a suspension of $[M(BMA)_2(H_2O)_2]$ (2 mmol) in 30 ml of acetone and the mixture was stirred under nitrogen for 24 h. The solid was filtered off, washed with acetone, and dried under vacuum; yield $\geq$ 95%. Anal. Found: C, 37.04; H, 2.90; N, 5.26. $C_{16}H_{14}N_2Br_2CoO_4$ calcd.: C, 37.16; H, 2.73; N, 5.42%; m.p. 192 °C. Found: C, 36.90; H, 2.68; N, 5.27. $C_{16}H_{14}N_2Br_2NiO_4$ calcd.: C, 37.18; H, 2.73; N, 5.42%; m.p. 201 °C.

AsPh$_4$[Fe(BMA)$_3$]. An aqueous solution (20 ml) of Na(BMA) (2.77 g, 16 mmol) was slowly added to a solution of $FeCl_2 \cdot 3\text{–}4H_2O$ (1 g, ca. 5 mmol) in 20 ml of water and the mixture was stirred for 24 h. Addition of $[AsPh_4]Cl \cdot H_2O$ (2.18 g, 5 mmol) caused precipitation of a red solid, which was filtered off and recrystallized from acetone (5 ml)/diethyl ether (30–40 ml). In some cases addition of ether to the acetone solution of the complex gave an oily product which, by vigorous stirring, generally afforded the red solid product; yield $\geq$ 55%. Anal. Found: C, 44.42; H, 3.03. $C_{33}H_{26}AsBr_3FeO_6$ calcd.: C, 44.58; H, 2.95%; m.p. 85 °C dec. Λ_M 56.4 $\Omega^{-1}M^{-1}cm^2$.

[FeBr(4-CH$_3$C$_6$H$_4$NC)$_5$]BPh$_4$. An excess of 4-tolyl isocyanide (0.94 ml, 8 mmol) in 20 ml of acetone was added to 0.39 g (1 mmol) of $[Fe(BMA)_2(H_2O)_2]$ and the mixture was refluxed for 8 h. After filtration, the solvent was removed under reduced pressure to give a brown oil which was treated with ethanol (10 ml). Addition of $NaBPh_4$ (0.34 g, 1 mmol) to the resulting solution gave a yellow solid which was filtered off and recrystallized from dichloromethane (5 ml)/diethyl ether (30 ml); yield $\geq$ 65%. Anal. Found: C, 73.55; H, 6.84; N, 6.60. $C_{64}H_{55}N_5BBrFe$ calcd.: C, 73.86; H, 5.33; N, 6.73%; m.p. 177 °C. Λ_M 51.9 $\Omega^{-1}M^{-1}cm^2$. $\delta(H)[(CD_3)_2CO]$ 7.39, 6.90 (40 H, m, $4C_6H_5$ and $5C_6H_4$) and 2.34, 2.29 (15 H, s, 5 CH_3).

CoBr$_2$(4-CH$_3$C$_6$H$_4$NC)$_4$. An excess of $4\text{-}CH_3C_6H_4NC$ (1.17 ml, 10 mmol) was added to a suspension of $Co(BMA)_2(H_2O)_2$ (0.79 g, 2 mmol) in 20 ml of acetone and the mixture was refluxed for 3 h under nitrogen. The resulting green solid was filtered off and recrystallized from CH_2Cl_2 (5 ml)/ethanol (20 ml); yield $\geq$ 60%. Anal. Found: C, 55.92; H, 4.09; N, 8.11; Br, 22.8. $C_{32}H_{28}N_4Br_2Co$ calcd.: C, 55.91; H, 4.11; N, 8.15; Br, 23.25%; m.p. 199 °C.

[Cu(4-CH$_3$C$_6$H$_4$NC)$_4$]Br. An excess of $4\text{-}CH_3C_6H_4NC$ (1.4 ml, 12 mmol) in 15

ml of acetone was added to 0.73 g (2 mmol) of Cu(BMA)$_2$ and the mixture was refluxed for 1 h. About half of the solvent was evaporated off, and the solution was filtered and cooled to $-30\,^{\circ}$C. White crystals separated out after 1 day and were filtered off and dried under vacuum; yield $\geq 60\%$. Anal. Found: C, 62.73; H, 4.59; N, 9.02; Br, 13.2. $C_{32}H_{28}N_4BrCu$ calcd.: C, 62.79; H, 4.61; N, 9.16; Br, 13.06%; m.p. 131°C. Λ_M 82.5 Ω^{-1} M^{-1} cm^2. δ(H)(CD_2Cl_2) 7.33 (16 H, m, 4 C_6H_4) and 2.39, 2.10 (12 H, s, 4 CH_3).

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