Unique keto-enol tautomerism in transition metal complexes of cyanoimidodithiocarbonate

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A novel potential bidentate sulfur ligand, $K_2[S_2CNHCOCH_2CN]$ and its complexes with first row divalent transition metal ions of the type, M(phen)L, [M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Pd(II), L = $S_2CNHCOCH_2CN$ and phen = 1,10-phenanthroline] have been synthesised and characterised. On the basis of IR and ^1H NMR an enol form is found in the case of ligand and its complexes in the solid state whereas the complexes exist predominantly in the keto form in solution. Electronic spectra and magnetic measurement data indicate that the Ni(II), Cu(II) and Pd(II) complexes have a square-planar geometry but the others have a distorted-tetrahedral structure.

Keywords: bidentate sulfur ligand, cyanoimidodithiocarbonate, 1,10-phenanthroline, keto-enol tautomerism

Hantzsch and Wolvekamp[1] reported the first synthesis of dimethyldibenzoylcyanoimidodithiocarbonate anion. To our knowledge only two complexes of cyanoimidodithiocarbonate have so far been crystallographically characterised, $[AsPh_4]_2[Ni(C_2N_2S_2)]$[2] and $[Au_2(C_2N_2S_2)]$.[3] The other known complexes bearing the $(C_2N_2S_2)^{2-}$ core, are $[SnR_2(C_2N_2S_2)]$, $[V(\eta^5\text{-}C_5H_5)(C_2N_2S_2)]$,[4] $[TcO(C_2N_2S_2)]$[5] and a series of a salt of the type $[M(C_2N_2S_2)]\,[X]_2$ where M = Ni, Pt, Pd, Zn or Tl and X = $AsPh_4$, PPh_4 or $P(Pr^n)_4P$.[6,7]

McFadyen[8,9] *et al.* reported a series of compounds with substituted phenanthroline and found them to be more effective against Murine Leukemia L1210 cell lines. In continuation of our work on sulfur-donor systems,[10-12] we herein report the synthesis and characterisation of a novel potassiumcyanoimidodithiocarbonato-salt and its interaction with $[MCl_2(phen)]$- type compounds.

Experimental

Hydrated metal chlorides, cyanoacetamide (BDH), carbondisulfide, and potassium hydroxide (Merck) were used as received. Methanol was used after distillation. Elemental analyses (C, H, N and S) were carried out with a Flash EA1112 Analyser, CE Instrument. IR spectra (4000–350 cm^{-1}) were recorded with an FT IR, Perkin-Elmer Spectrum BX as KBr discs. The conductivity measurements were carried out with a CM-82T Elico conductivity bridge in DMSO. The electronic spectra were recorded with a Cintra 5GBC spectrophotometer in DMSO. Magnetic susceptibility measurements were done with a Sherwood Scientific MSB Auto at room temperature. TGA/DSC was performed with a Universal V3.8 B TA SDT Q600 Build 51 Thermal Analyser. The experiment was carried out under a dinitrogen atmosphere using alumina powder as reference. The heating rate was kept at 20°C/min and the metal contents were estimated by complexometric titration.[13]

Synthesis of $K_2S_2CNCOHCHCN$ (K_2L)

To a methanolic solution (25 ml) of cyanoacetamide (25 mmol, 2.10 g) kept in an ice bath, was added carbondisulfide (25 mmol, 1.51 ml) dropwise, with continuous stirring over a period of 15 minutes. To this reaction mixture, KOH (50 mmol, 2.8 g) in 25 ml methanol was added and the mixture was stirred for six hours, which yielded a yellow precipitate. It was decanted, washed with methanol and ether and dried *in vacuo* over $CaCl_2$. The compound is hygroscopic in nature. Yield, 90%

Synthesis of $[CuCl_2(phen)]$

To a cold methanolic solution (100 ml) of 1,10-phenanthroline (1.98 g, 10 mmol), hydrated $CuCl_2$ (10 mmol, 1.7 g) in 50 ml methanol was slowly added, which afforded brisk precipitation of a green complex. It was filtered, washed with cold methanol and dried *in vacuo*. Yield, 93%.

$[PdCl_2(phen)]$ was also synthesised by the above procedure. Yield, 92%.

Synthesis of $[MCl_2(phen)]$

Hydrated MCl_2 (10 mmol) {where M = Mn(II), Fe(II), Co(II) and Ni(II)} in 50 ml methanol was slowly added to a methanolic solution (50 ml) of 1,10-phenanthroline (1.98 g, 10 mmol). The mixture was stirred for half an hour and reduced to half by evaporation. It was left for three to four days to yield the respective precipitate. The solid was washed with methanol, ether and dried *in vacuo*. Yield, 88% $\{Ni(phen)Cl_2\}$; 76% $\{Co(phen)Cl_2\}$ and 73% $\{Mn(phen)Cl_2\}$.

Synthesis of [ML(phen)] {where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Pd(II) }

To a well-stirred methanolic solution (25 ml) of $K_2[S_2CNCOHCHCN]$ (2.36 g, 10 mmol) was added $[MCl_2(phen)]$ (10 mmol) in the same solvent (20 ml). The reaction mixture was refluxed on a hot plate, with continuous stirring, for about 4 hours. It was left overnight and the resulting precipitate was filtered off, washed with methanol, diethyl ether and dried *in vacuo*.

Results and discussion

The complexes of the type [ML(phen)] {where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Pd(II), L = $[S_2CNCOHCHCN]$ and phen = 1,10-phenanthroline} are formed by the replacement of two chlorine atoms from $[MCl_2(phen)]$ by $K_2[S_2CNCOHCHCN]$ (Fig. 1). They are stable to light, soluble in DMSO, DMF and are amorphous in nature.

$$[MCl_2(phen)] + K_2[S_2CNCOHCHCN] \rightarrow [ML(phen)] + 2KCl$$

The molar conductivity of 10^{-3} M solution of the complexes measured in DMSO indicated their non-electrolytic nature (Table 1).[14]

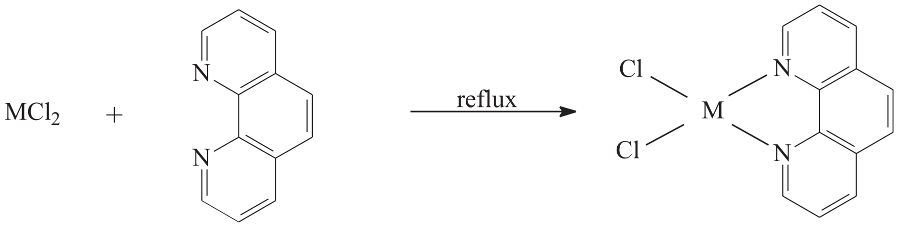

Fig. 1 Synthesis of MCl_2(phen) where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Pd(II) and phen = 1,10-phenanthroline.

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Table 1 Analytical data and physical properties of the complexes

Compounds (F.W)	Colour	M. p./°C	Yield/%	Molar conductance /ohm^{-1}mol^{-1}cm^{2}	Analysis (%) Found (calcd)				
					C	H	N	S	M
K_2L	Yellow	110	90	–	20.1	0.7	11.75	27.3	–
(236.39)					(20.32)	(0.85)	(11.85)	(27.12)	
Mn(phen)L	Light brown	140	55	13.1	48.7	2.4	14.1	16.5	13.8
(393.34)					(48.86)	(2.56)	(14.24)	(16.30)	(13.97)
Fe(phen)L	Dark brown	260	62	32.5	48.5	2.4	14.1	16.5	14.1
(394.25)					(48.74)	(2.55)	(14.21)	(16.26)	(14.16)
Co(phen)L	Green	180	67	17.2	48.2	2.4	13.9	16.3	14.9
(397.34)					(48.37)	(2.54)	(14.10)	(16.14)	(14.83)
Ni(phen)L	Algae green	225	70	31.7	48.2	2.4	13.9	16.3	14.5
(397.11)					(48.39)	(2.54)	(14.11)	(16.15)	(14.78)
Cu(phen)L	Yellow	288	68	10.8	47.7	2.4	13.8	15.7	16.1
(401.95)					(47.81)	(2.51)	(13.94)	(15.95)	(15.81)
Pd(phen)L					43.0	2.0	12.4	14.5	24.05
(444.80)	Yellow	105	55	8.7	(43.20)	(2.26)	(12.59)	(14.41)	(23.92)

IR spectra

In the ligand a strong nitrile band ($C\equiv N$) is observed at 2177 cm^{-1} while for the complexes it appears in the 2177–2218 cm^{-1} range which is characteristic of the conjugated cyano group ($C\equiv N$) in the open chain and heterocyclic derivatives.[15] The imido-band (C=N) was observed at 1460 cm^{-1} in the case of uncoordinated cynaoimidodithiocarbamato-dianion and is shifted to higher frequency in the complexes (1474–1486 cm^{-1}), implying the delocalisation of the electron cloud over the S_2CN region.[16] In addition, a strong band is also observed at 3400 due to ν(O–H) implying the existence of the enol form in the solid state, and remains unaltered.[17] However, in case of the uncoordinated 1,10-phenanthroline molecule, two groups of doublets were observed due to the strong interaction between C=C and C=N which are shifted to lower wave numbers on coordination. We have also observed two strong doublets in the same region.[18] The strong bands at 846–838 cm^{-1} and 723–729 cm^{-1} range were assigned to CH out-of-plane bend (two adjacent), ring breathing and deformation absorptions of coordinated 1,10-phenantroline molecule respectively.[19] Some new bands of weak intensity are also observed in 409–431 cm^{-1} range corresponding to ν(M–N).[20]

Electronic spectra and magnetic moments

The deep yellow solution of the [MnL(phen)] complex in DMSO exhibits strong charge transfer at 33, 334 and 31, 250 cm^{-1} characteristic of tetrahedral Mn(II) ion besides an additional band at 19,230 cm^{-1} assigned to the $^4T_1 \leftarrow {}^6A_1$ transition. The magnetic moment (5.62 B.M.) also supports a tetrahedral geometry for the Mn(II) ion.[21]

The tetrahedral high-spin Fe(II) complex shows one spin-allowed d–d band at 23,529 cm^{-1} corresponding to the $^5E \leftarrow {}^5T_2$ transition. The magnetic moment for tetrahedral Fe(II) complexes lies between 5.0 and 5.5 B.M. corresponding to four unpaired electrons and we have obtained a value of 5.05 B.M. which is consistent with the tetrahedral nature[22] of this Fe(II) ion.

For the tetrahedral Co(II) complexes two bands are observed at 15,600 and 22,471 cm^{-1} corresponding to $^4T_2(F) \leftarrow {}^4A_2(F)$ and $^4T_1(F) \leftarrow {}^4A_2(F)$ transitions, respectively, in addition to a charge transfer at 27, 000 cm^{-1}. Generally, the magnetic moment of tetrahedral,[23] Co(II) complexes lies in the range 4.2–4.7 B.M. while for octahedral Co(II) it falls between 4.4–5.5 B.M. The observed magnetic moment (4.38 B.M.) and the ligand field spectrum suggest a tetrahedral geometry for the Co(II) ion.

Two high intensity d–d transitions are observed at 15,503 and 23,696 cm^{-1} corresponding to the $^1A_{2g} \leftarrow {}^1A_{1g}$ and $^1B_{1g} \leftarrow {}^1A_{1g}$ transitions, respectively in the case of the Ni(II) complex, supporting a square-planar structure.[24] However, in the case of the diamagnetic complex [PdL(phen)] a strong d–d band observed at 17,500 cm^{-1} supports a square-planar structure for the complex.[25]

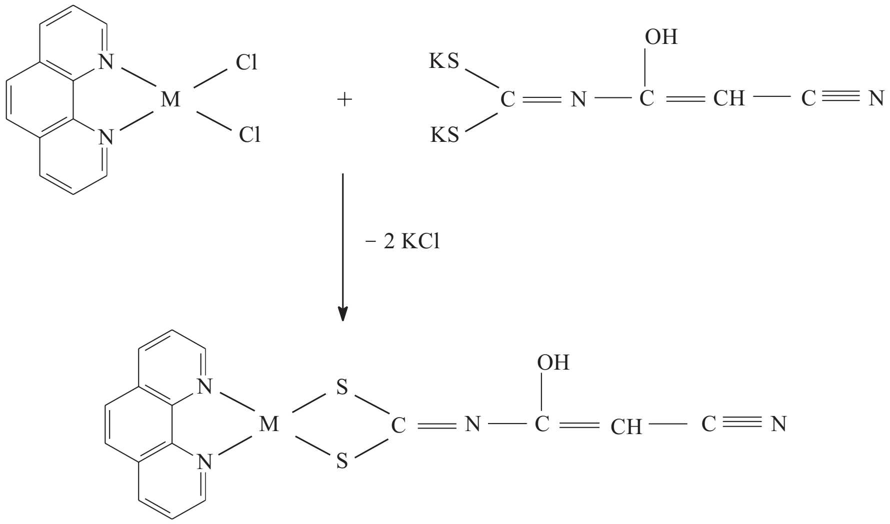

Fig. 2 Synthesis of M(phen)L where L = $S_2CNCOHCHCN$, M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Pd(II) and phen = 1,10-phenanthroline.

The green Cu(II) complex shows two d–d absorption bands at 23,529 and 14,814 cm^{-1} corresponding to $^2A_{1g} \leftarrow {}^2B_{1g}$ and $^2E_g \leftarrow {}^2B_{1g}$ transitions, respectively and a charge transfer band at 24,570 cm^{-1}. It is well known that for square-planar Cu(II) complexes the magnetic moment value falls in the range 1.82–1.86 B.M. while for a tetrahedral Cu(II) ion, the μ_{eff} is slightly higher (1.92–2.00 B.M.).[26] A value of 1.83 B.M. for Cu(II) ion has been observed which is well within the expected region found for square-planar Cu(II) complexes.

TGA/DSC

The ligand decomposition profile exhibits two steps which are not well separated. The first stage (60–400°C) corresponds to the loss of two potassium ions (found 33.10, calcd. = 33.08 wt %). The second stage of degradation occurs from 400 to 800°C leading to the pyrolysis of the remaining part of the molecule. From the DSC curve it is inferred that the first step of decomposition is a combination of a sharp endothermic minima followed by a broad exothermic hump. However, the second process is purely an exothermic one.[27]

Since all the complexes have identical environment, the TGA/DSC of only Mn, Fe and Pd-complexes have been scanned. All the complexes have three well defined decomposition stages. The first stage is sharp and steep which is ascribable to the removal of phenanthroline.[28] The process is exothermic in nature as depicted in their DSC curve. The second stage corresponds to the decomposition of remaining organic moiety of the molecule while the third stage is consistent with the formation of respective metal sulfide.[29] The DSC plots of the complexes shows that the decomposition of organic moiety is an exothermic process while a flat line is observed for the formation of metal sulfide as residue.

^{1}H NMR

The ligand $K_2[S_2CNCOHCHCN]$, exhibits a sharp singlet at 3.75 ppm due to the methine proton while the hydroxy proton was observed at 10.72 ppm. Another strong singlet was observed at 3.25 ppm suggesting the presence of methylene protons in DMSO (Table 2). The integration of protons in the ligand for methine, hydroxy and methylene protons was found to be 1 : 1 : 2 implying the predominance of the keto-form in solution. This fact is also supported by the polar nature of DMSO.[30] However, the complexes show a singlet at about 3.24 ppm due to methylene protons and multiplets ranging from 7.64 to 9.00 ppm attributing to phenanthroline protons.[31] The protons adjacent to nitrogen atoms (2H) appear as a doublet at 9.00 ppm. Two vinylic type protons (2H) of the phenanthroline appear as a singlet at 7.67 ppm, whereas the *meta*-protons (2H) were found to resonate as a double-doublet at 8.40 ppm (J = 1–2). Moreover, there is no peak corresponding to hydroxyl protons indicating the presence of the keto-form in the complexes.

The authors are grateful to Prof. M. Mushfiq and M. Alam, Department of Chemistry for a fruitful discussion on ^{1}H NMR.

Table 2 ^{1}H NMR of the ligand and its complexes

Complexes	δ(CH)	δ(CH_2)	δ(OH)	δ(phen)
K_2L	3.75 s	3.25 s	10.72 s	–
[MnL(phen)]	–	3.24 s	–	7.64–9.00 m
[FeL(phen)]	–	3.25 s	–	7.60–9.00 m
[CoL(phen)]	–	3.24 s	–	7.64–8.94 m
[NiL(phen)]	–	3.24 s	–	7.70–9.00 m
[CuL(phen)]	–	3.23 s	–	7.54–8.98 m
[PdL(phen)]	–	3.25 s	–	7.64–9.00 m

One of us (SAAN) thanks the Department of Chemistry, Aligarh Muslim University, Aligarh (India) for the award of a research fellowship.

Received 3 January 2006; accepted 3 April 2006
Paper 06/3731

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