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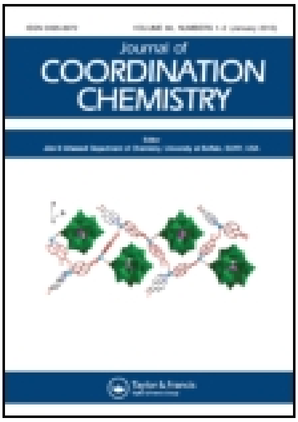

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

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Published online: 14 Jun 2013.

To cite this article: Keo Vanthoeun, Haruka Yamazaki, Takayoshi Suzuki & Masakazu Kita (2013) Preparation and molecular structures of N,N-2,2′-dipicolyl- and N,N-3,3′-dipicolyldithiocarbamato metal complexes, Journal of Coordination Chemistry, 66:13, 2378-2387, DOI: 10.1080/00958972.2013.804914

To link to this article: http://dx.doi.org/10.1080/00958972.2013.804914

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Journal of Coordination Chemistry, 2013
Vol. 66, No. 13, 2378–2387, http://dx.doi.org/10.1080/00958972.2013.804914

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Preparation and molecular structures of *N,N*-2,2′-dipicolyl- and *N,N*-3,3′-dipicolyldithiocarbamato metal complexes

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(*Received 28 November 2012; in final form 21 March 2013*)

New iron(III) and cobalt(III) complexes, [Fe(2,2′-dpdtc)$_3$], [Fe(3,3′-dpdtc)$_3$], [Co(2,2′-dpdtc)$_3$], and [Co(3,3′-dpdtc)$_3$] (dpdtc = dipicolyldithiocarbamate) have been synthesized and their molecular structures and spectroscopic properties determined. The 2,2′- and 3,3′-dpdtc ligands have four donors, S, S′, N, and N′. These complexes are insoluble in water, but soluble in acidic solution. Crystal structures of these metal complexes reveal that the central metal ions have MS$_6$ (M = Fe and Co) octahedral structures and all dipicolyl groups do not coordinate.

Keywords: Iron(III) and cobalt(III) complexes; Crystal structure; *N,N*-2,2′-Dipicolyl; *N,N*-3,3′-dipicolyldithiocarbamates

1. Introduction

Dithiocarbamato metal complexes have been extensively studied [1]. Dithiocarbamates are bidentate ligands through sulfur and a number of transition metal dithiocarbamato complexes have been studied and characterized [2–8]. Synthesis and characterization of *N,N*-diacetatodithiocarbamato metal complexes with large negative charges has been reported [9]. The ligand, 2,2′-dpdtc has been studied as a spontaneously assembling dithiocarbamate on gold surface [10], but there are no reports of metal complexes with the new ligands, *N,N*-2,2′-dipicolyl- and *N,N*-3,3′-dipicolyldithiocarbamate. We have designed these ligands as bridges for polynuclear complexes. Possible bonding modes are through two sulfurs and two picolyl nitrogens and these ligands can bridge with different metals to form polynuclear complexes.

In this paper, we synthesized *N,N*-2,2′-dipicolyl- and *N,N*-3,3′-dipicolyldithiocarbamato iron(III) and cobalt(III) complexes, [Fe(2,2′-dpdtc)$_3$], [Fe(3,3′-dpdtc)$_3$], [Co(2,2′-dpdtc)$_3$], and [Co(3,3′-dpdtc)$_3$]. Our interest, in these complexes is due to the possibility for different coordination structures and properties with the position of picolyl groups. Moreover, these metal complexes can be used as indicators in acidic solutions caused by their deep color in acidic media.

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2. Experimental

2.1. *Materials*

Complexes of [Fe(2,2′-dpdtc)$_3$], [Fe(3,3′-dpdtc)$_3$], [Co(2,2′-dpdtc)$_3$], and [Co(3,3′-dpdtc)$_3$] were prepared using procedures similar to those in the literature [11, 12]. The chemicals, 2,2′-dipicolylamine, 3,3′-dipocolylamine, carbon disulfide (CS_2), and chloroform ($CHCl_3$) were purchased from Tokyo Chemical Industry and Nacalai Tesque Inc.

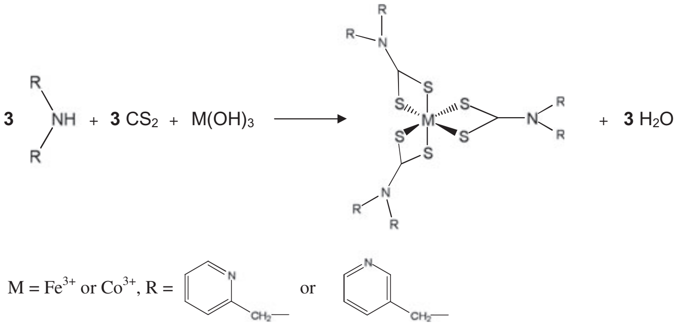
2.2. *Preparation of metal complexes*

2.2.1. Fe(OH)$_3$ and Co(OH)$_3$. $FeCl_3 \cdot 6H_2O$ and NaOH were mixed in the molar ratio 1 : 3 in water, affording a reddish precipitate of $Fe(OH)_3$. The precipitate was collected by repeated centrifugation and was washed with distilled water. $CoCl_2 \cdot 6H_2O$ and NaOH were mixed in the molar ratio 1 : 3 in water, producing a bluish precipitate of $Co(OH)_2$. Three percent of hydrogen peroxide (H_2O_2) solution was slowly added to the mixture in the stoichiometric ratio 1 : 0.5, producing a greenish precipitate of $Co(OH)_3$. The precipitate was collected by repeated centrifugation and was washed with distilled water.

2.2.2. Synthesis of dithiocarbamato metal complexes

2.2.2.1. [Fe(2,2-dpdtc)$_3$]. 2.50 g (13.0 mM) of 2,2′-dipicolylamine and 1.00 g (13.0 mM) of CS_2 were dissolved separately in 10.0 mL of MeOH. Both solutions were added, with stirring, into a MeOH solution suspension containing freshly prepared $Fe(OH)_3$ (4.30 mM) (scheme 1). After stirring for 5 min, black precipitates were deposited and then collected by filtration. Yield: 2.00 g (50%). Anal. Calcd for [Fe(2,2′-dpdtc)$_3$] (%) = $C_{39}H_{36}N_9S_6Fe$: C, 53.7; H, 4.13; N, 14.4. Found: C, 52.5; H, 3.60; N, 14.1.

2.2.2.2. [Fe(3,3′-dpdtc)$_3$]. This complex was prepared by using 3,3′-dipicolylamine instead of 2,2′-dipicolylamine, following similar procedure (2.2.2.1). Yield: 2.5 g (63%). Anal. Calcd for black compound of [Fe(3,3′-dpdtc)$_3$]·H_2O (%) = $C_{39}H_{38}N_9OS_6Fe$: C, 52.2; H, 4.27; N, 14.1. Found: C, 52.6; H, 4.01; N, 14.0.



Scheme 1. Synthesis of *N,N*-2,2′-dipicolyl- and *N,N*-3,3′-dipicolyldithiocarbamato complexes of iron(III) and cobalt(III).

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2.2.2.3. [Co(2,2′-dpdtc)$_3$]. This complex was prepared similarly to the method in [Fe(2,2′-dpdtc)$_3$] by using Co(OH)$_3$ instead of Fe(OH)$_3$. Yield: 2.1 g (53%). A green compound was collected by filtration. Anal. Calcd for [Co(2,2′-dpdtc)$_3$] (%) = $C_{39}H_{36}N_9S_6Co$: C, 53.1; H, 4.11; N, 14.2. Found: C, 51.7; H, 3.76; N, 14.0.

2.2.2.4. [Co(3,3′-dpdtc)$_3$]. [Co(3,3′-dpdtc)$_3$] was prepared in a similar procedure to that of [Co(2,2′-dpdtc)$_3$] by using 3,3′-dipicolylamine instead of 2,2′-dipicolylamine. Yield: 2.4 g (60%). Anal. Calcd for green compound of [Co(3,3′-dpdtc)$_3$]·H_2O (%) = $C_{39}H_{38}N_9OS_6Co$: C, 52.0; H, 4.40; N, 13.7. Found: C, 52.9; H, 3.71; N, 14.0.

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2.3. *Crystallography*

Crystallographic and structural refinement data for [Fe(2,2′-dpdtc)$_3$], [Fe(3,3′-dpdtc)$_3$]·H_2O, [Co(2,2′-dpdtc)$_3$], and [Co(3,3′-dpdtc)$_3$]·H_2O are listed in table 1. A black prismatic crystal of [Fe(2,2′-dpdtc)$_3$] with approximate dimensions of 0.30 × 0.20 × 0.20 mm and a black prismatic crystal of [Fe(3,3′-dpdtc)$_3$]·H_2O (approximately 0.20 × 0.20 × 0.20 mm) were each mounted using a cryoloop and liquid paraffin, and flash-cooled with a cold nitrogen stream. X-ray diffraction data ($6° < 2\theta < 55°$) were obtained at -80 ± 1 °C on a Rigaku Varimax 724 diffractometer with multi-layer mirror monochromated Mo–Kα radiation ($\lambda = 0.71075$ Å).

A green platelet crystal of [Co(2,2′-dpdtc)$_3$] with approximate dimensions of 0.35 × 0.20 × 0.10 mm was glued to the top of a glass fiber and mounted on a Rigaku R-axis rapid and analyzed using graphite monochromated Mo–K*α* radiation ($\lambda = 0.71075$ Å). X-ray diffraction data ($8° < 2\theta < 55°$) were obtained at 23 ± 1 °C.

A green platelet crystal of [Co(3,3′-dpdtc)$_3$]·H_2O with approximate dimensions of 0.35 × (0.20 × 0.20 mm was mounted using a cryoloop and liquid paraffin, and flash

Table 1. Crystallographic and structure refinement data.

Complexes	[Fe(2,2′-dpdtc)$_3$]	[Fe(3,3′-dpdtc)$_3$]·H_2O	[Co(2,2′-dpdtc)$_3$]	[Co(3,3′-dpdtc)$_3$]·H_2O
Formula	$C_{39}H_{36}FeS_6N_9$	$C_{39}H_{38}FeS_6ON_9$	$C_{39}H_{36}CoS_6N_9$	$C_{39}H_{38}CoS_6ON_9$
Formula weight	878.98	896.99	882.06	900.07
Color	Black	Black	Green	Green
T/°C	−80 (1)	−80 (1)	23 (1)	−87 (1)
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Z	2	4	2	2
a (Å)	7.968(2)	19.0661(15)	7.9361(13)	10.9326(10)
b (Å)	11.293(3)	7.9907(4)	11.410(2)	14.0321(11)
c (Å)	23.298(6)	27.851(2)	23.418(4)	14.9484(14)
α (°)	79.454(6)	90	79.252(5)	116.250(3)
β (°)	86.899(8)	93.892(4)	86.346(5)	96.855(2)
γ (°)	77.439(7)	90	76.376(5)	96.600(3)
V (Å^3)	2011.5(9)	4233.5(5)	2024.2(6)	2005.4(3)
D_{calc} (g/cm^3)	1.451	1.407	1.447	1.520
F(000)	910	1860	912	932
R_{int}	0.033	0.067	0.032	0.027
μ (MoKα) (cm^{-1})	7.283	6.953	7.756	7.862
$R_1(I > 2(I))$	0.0324	0.0649	0.0380	0.0393
wR_2 (all reflections)	0.0872	0.1915	0.1194	0.1229
Goodness of fit on F^2	1.045	1.145	1.092	1.135

cooled with a cold nitrogen gas stream. X-ray diffraction data were obtained at −87 ± 1 °C using a Rigaku R-axis rapid imaging plate area detector with graphite monochromated Mo–Kα radiation ($\lambda = 0.71075$ Å).

All structural calculations were carried out using the Crystal Structure software package [13]. The structures were solved by direct methods using the SIR 2004 software package [14] and refined on F^2 (with all independent reflections) using SHELXL 97 [15]. All non-hydrogen atoms were refined anisotopically. Hydrogens of dpdtc were introduced at calculated positions and treated using the riding model on the attached C, while those of the hydrated waters were not included in the calculation.

2.4. *Measurements*

UV–vis absorption spectra of [Fe(2,2′-dpdtc)$_3$], [Fe(3,3′-dpdtc)$_3$], [Co(2,2′-dpdtc)$_3$], and [Co(3,3′-dpdtc)$_3$] in $CHCl_3$ solution were measured using a Hitachi U-3900H spectrophotometer. The solubility of these complexes was measured in hydrochloric acid solution adjusted to different pHs (pH 1–7). The mixture of a metal complex and an acidic solution was stirred for an hour and the resulting mixture was filtered off using a glass microfibre filter (GFA, Whatman, 25 mm diameter). The absorbance of the filtrate was measured at 490 and 650 nm for Fe(III) and Co(III) complexes, respectively. [Fe(3,3′-dpdtc)$_3$] decomposed in acidic aqueous solution.

3. Results and discussion

N,N-2,2′-dipicolyl- and *N,N*-3,3′-dipicolyldithiocarbamato metal complexes were synthesized by reaction of 2,2′-dipicolylamine or 3,3′-dipicolylamine and CS_2 with $Fe(OH)_3$ or $Co(OH)_3$ in the stoichiometric molar ratio 3 : 3 : 1 (amine: CS_2: $M(OH)_3$). The resulting complexes were [Fe(2,2′-dpdtc)$_3$], [Fe(3,3′-dpdtc)$_3$], [Co(2,2′-dpdtc)$_3$], and [Co(3,3′-dpdtc)$_3$]. These metal complexes are insoluble in water, but soluble in methanol, ethanol, chloroform, and dimethyl sulfoxide. They were recrystallized from a chloroform solution by slowly mixing with diethyl ether vapor in a closed vessel.

Figures 1–4 illustrate the molecular structures of [Fe(2,2′-dpdtc)$_3$], [Fe(3,3′-dpdtc)$_3$], [Co (2,2′-dpdtc)$_3$], and [Co(3,3′-dpdtc)$_3$], respectively. The structures of [Fe(2,2′-dpdtc)$_3$], [Co (2,2′-dpdtc)$_3$], and [Co(3,3′-dpdtc)$_3$]·H_2O crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$ and [Fe(3,3′-dpdtc)$_3$]·H_2O crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$.

Tables 2 and 3 list selected average bond lengths and bond angles of these complexes. Coordination of these complexes are normal tris(dithiocarbamate) MS_6 structures. The dipicolyl groups do not coordinate. The S–Fe–S and S–Co–S bond angles are similar to those of tris(*N,N*-diethyldithiocarbamato)iron(III) ([Fe(Et$_2$dtc)$_3$]) [16] and tris(*N,N*-diethyldithiocarbamato)cobalt(III) ([Co(Et$_2$dtc)$_3$]) [17].

Absorption spectra of [Fe(2,2′-dpdtc)$_3$], [Fe(3,3′-dpdtc)$_3$], [Co(2,2′-dpdtc)$_3$], and [Co (3,3′-dpdtc)$_3$] in chloroform are shown in figure 5 and the spectral data are listed in table 4. The iron(III) complexes with 2,2′-dpdtc and 3,3′-dpdtc show a typical FeS_6 chromophore. The lower energy transitions at 16,250 and 19,500 cm^{-1} are similar in energy to those of [Fe(Et$_2$dtc)$_3$] reported by Kunkely and Vogler [18] and Miessler *et al.* [19]. Thecobalt(III) complexes with 2,2′-dpdtc and 3,3′-dpdtc show a typical CoS_6 chromophore. The lower energy transitions at 16,150 and 20,500 cm^{-1} are similar to those found in absorption spectra of Na$_6$[Co(Ac$_2$dtc)$_3$] reported by Vanthoeun *et al.* [9].

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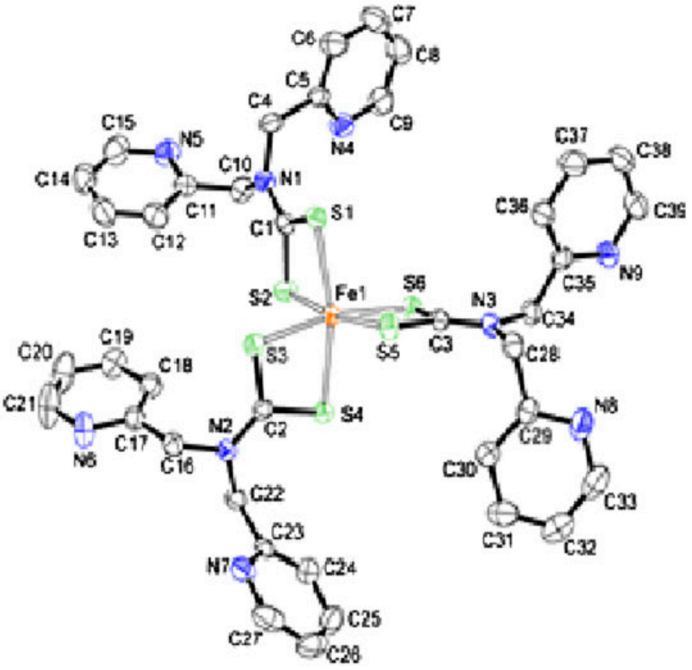

Figure 1. Molecular structure of [Fe(2,2′-dpdtc)$_3$].

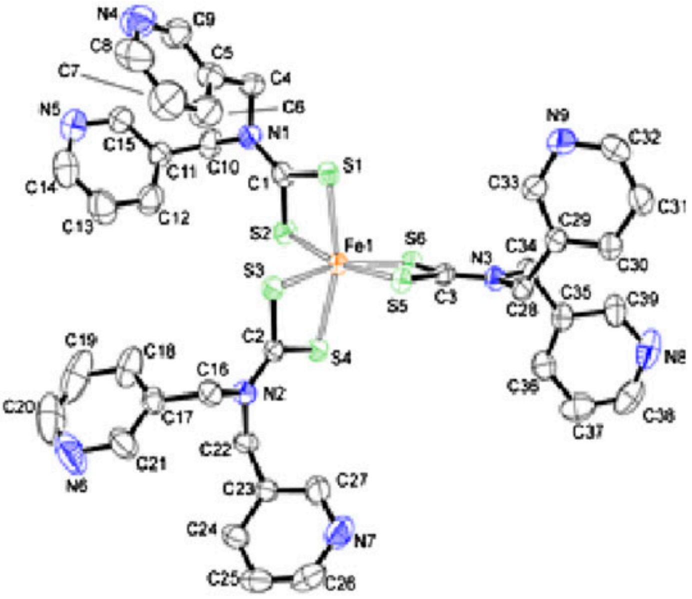

Figure 2. Molecular structure of [Fe(3,3′-dpdtc)$_3$].

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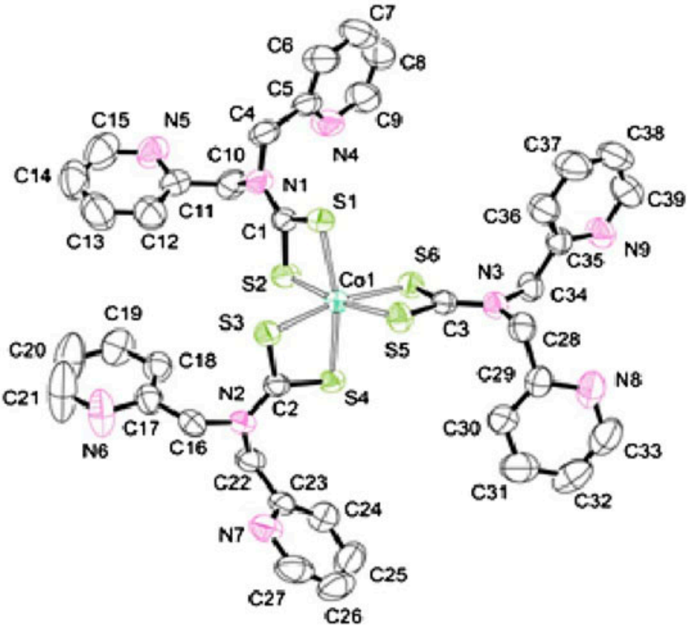

Figure 3. Molecular structure of [Co(2,2′-dpdtc)$_3$].

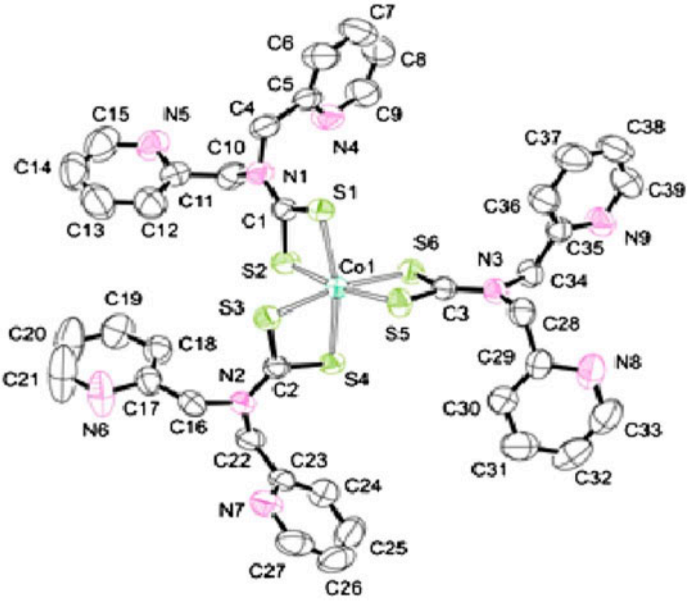

Figure 4. Molecular structure of [Co(3,3′-dpdtc)$_3$].

The solubilities of the complexes were determined by absorbance based on the Beer-Lambert law using a molar absorption coefficient in table 5. The *N,N*-2,2′-dipicolyl- and *N,N*-3,3′-dipicolyldithiocarbamato iron(III) and cobalt(III) complexes are insoluble in

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Table 2. Selected average bond lengths (Å).

Bond length	M–S	S–C	(C)N–C(S)	(C)N–C(C)	Ref.
[Fe(2,2′-dpdtc)$_3$]	2.311(5)	1.719(8)	1.324(8)	1.368(2)	This work
[Fe(3,3′-dpdtc)$_3$]	2.301(8)	1.714(3)	1.329(4)	1.3797(5)	This work
[Fe(Et$_2$dtc)$_3$]	2.309(1)	1.720(4)	1.326(6)	1.480(7)	[16]
[Co(2,2′-dpdtc)$_3$]	2.267(8)	1.707(3)	1.325(3)	1.387(4)	This work
[Co(3,3′-dpdtc)$_3$]	2.265(9)	1.709(3)	1.335(4)	1.378(6)	This work
[Co(Et$_2$dtc)$_3$]	2.268(8)	1.706(7)	1.315(15)	1.345(14)	[17]

Table 3. Selected average bond angles (°).

Bond angle	S–M–S	M–S–C	S–C–S	S–C–N	N–C–C	Ref.
[Fe(2,2′-dpdtc)$_3$]	75.59(7)	86.47(6)	111.2(8)	124.5(4)	117.6(6)	This work
[Fe(3,3′-dpdtc)$_3$]	75.69(3)	86.43(5)	110.8(8)	124.5(2)	120.2(4)	This work
[Fe(Et$_2$dtc)$_3$]	75.91(1)	86.51(1)	110.9(2)	124.3(2)	111.6(5)	[16]
[Co(2,2′-dpdtc)$_3$]	76.51(2)	86.24(10)	110.6(14)	124.6(2)	121.6(2)	This work
[Co(3,3′-dpdtc)$_3$]	76.62(3)	86.23(10)	110.6(12)	124.7(2)	121.4(2)	This work
[Co(Et$_2$dtc)$_3$]	76.50(1)	86.30(3)	110.9(3)	124.5(3)	112.6(11)	[17]

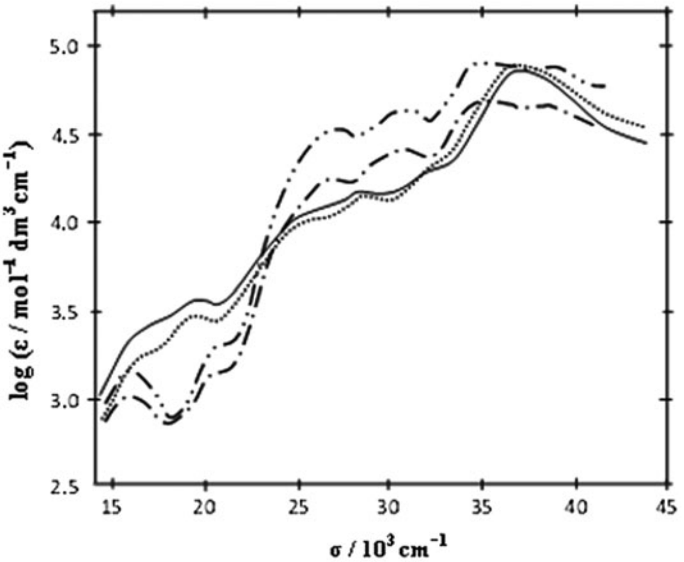

Figure 5. Absorption spectra of (…) [Fe(2,2′-dpdtc)$_3$], (—) [Fe(3,3′-dpdtc)$_3$], (– ▪ –) [Co(2,2′-dpdtc)$_3$], (–▪▪ –) [Co(3,3′-dpdtc)$_3$] in chloroform.

water, but soluble in hydrochloric acid. Table 6 lists the absorbance values at saturated solution and solubility of each metal complex at pH 1–7. Figure 6 shows the absorbance was rapidly increased below pH 2. Figures 7 and 8 show rapid increase below pH 2 of Fe (III) and Co(III) complexes, respectively. The high solubility of these metal complexes in acidic aqueous solution below pH 2 is caused by protonations of the dipicolyl nitrogens.

Table 4. Absorption spectral data.

Complexes	$\sigma/10^3$ cm^{-1} (log (ε/cm^{-1} M^{-1} dm^3))					Ref.
$[Fe(2,2'\text{-dpdtc})_3]$	16.25(3.45)	19.50(3.65)	21.0(3.60)^{sh}	28.50(4.27)	37.0(4.95)	This work
$[Fe(3,3'\text{-dpdtc})_3]$	16.25(3.35)	19.50(3.55)	21.0(3.55)^{sh}	28.50(4.25)	37.0(5.00)	This work
$[Fe(Et_2dtc)_3]$	16.94	19.45^{sh}	25.70	28.57	34.96	[18]
$[Co(2,2'\text{-dpdtc})_3]$	16.10(3.20)	18.50(3.0)^{sh}	20.05(3.35)	27.0(4.60)	30.05(4.60)	This work
$[Co(3,3'\text{-dpdtc})_3]$	16.10(3.25)	18.50(3.05)^{sh}	20.05(3.40)	27.0(4.45)	30.05(4.75)	This work
$Na_6[Co(Ac_2dtc)_3]$	15.8(2.79)	18.5(2.31)^{sh}	25.3(4.05)	30.8(4.43)	36.3(4.2)	[9]

^{sh}: shoulder.

Table 5. Absorption spectral data in acidic media (pH 1).

Complexes	$\sigma/10^3$ cm^{-1} (log (ε/cm^{-1} mol^{-1} dm^3))					
$[Fe(2,2'\text{-dpdtc})_3]$	18.5(2.55)	22.5(3.25)	30.0(3.60)	34.0(3.90)	–	–
$[Co(2,2'\text{-dpdtc})_3]$	16.1(2.25)	18.50(2.10)^{sh}	20.0(2.30)	27.0(3.45)	28.0(3.40)^{sh}	30.0(3.55)
$[Co(3,3'\text{-dpdtc})_3]$	16.1(2.35)	18.50(2.15)^{sh}	20.0(2.35)	27.0(3.55)	28.0(3.50)^{sh}	30.0(3.75)

^{sh}: shoulder.

Table 6. Absorbance and concentration of metal complexes in aqueous HCl solution at their saturation.

	$[Fe(2,2'\text{-dpdtc})_3]$		$[Co(2,2'\text{-dpdtc})_3]$		$[Co(3,3'\text{-dpdtc})_3]$	
pH	Abs at 490 nm	[C] mM	Abs at 650 nm	[C] mM	Abs at 650 nm	[C] mM
1	4.4100	2.479	6.8200	38.35	13.650	60.97
2	0.9950	0.559	3.1250	17.54	3.7000	16.52
3	0.0640	0.035	0.3890	2.187	0.7900	3.528
4	0.0460	0.025	0.0170	0.095	0.1400	0.625
5	0.0320	0.018	0.0110	0.062	0.0400	0.178
6	0.0220	0.012	0.0010	0.006	0.0040	0.0.17
7	–	–	–	–	–	–

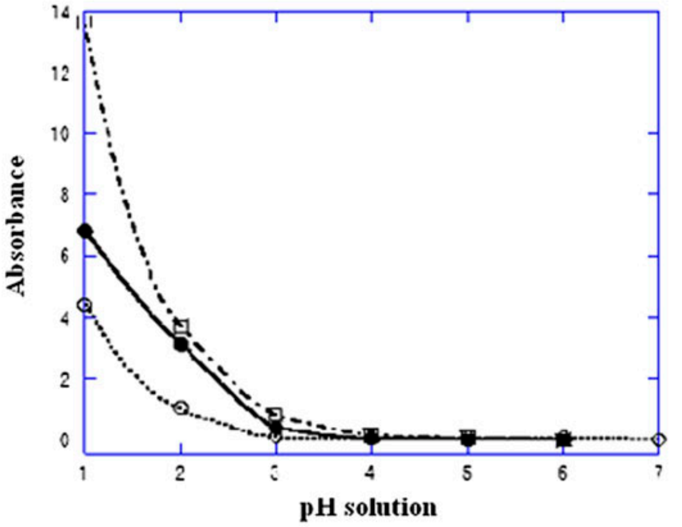

Figure 6. Absorbane of metal complexex with pHs (pH 0–7) (○) $[Fe(2,2'\text{-dpdtc})_3]$ (at 490 nm), (●) $[Co(2,2'\text{-dpdtc})_3]$ and (□) $[Co(3,3'\text{-dpdtc})_3]$ (at 650 nm).

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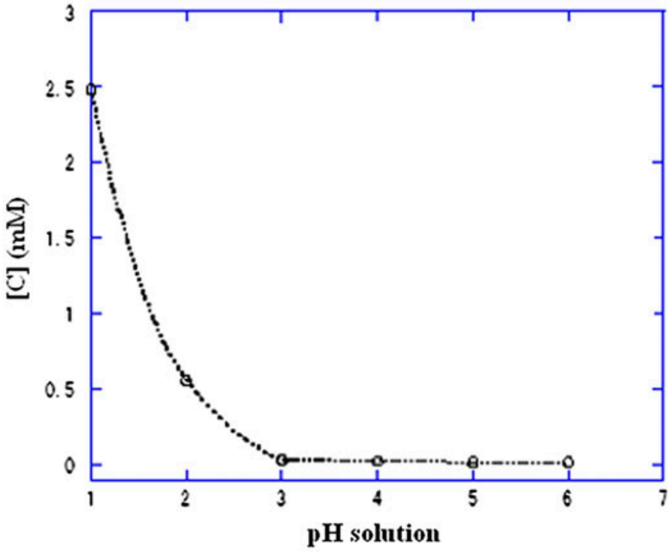

Figure 7. Determination of solubility of (○) [Fe(2,2′-dptc)$_3$ in pH 1–7.

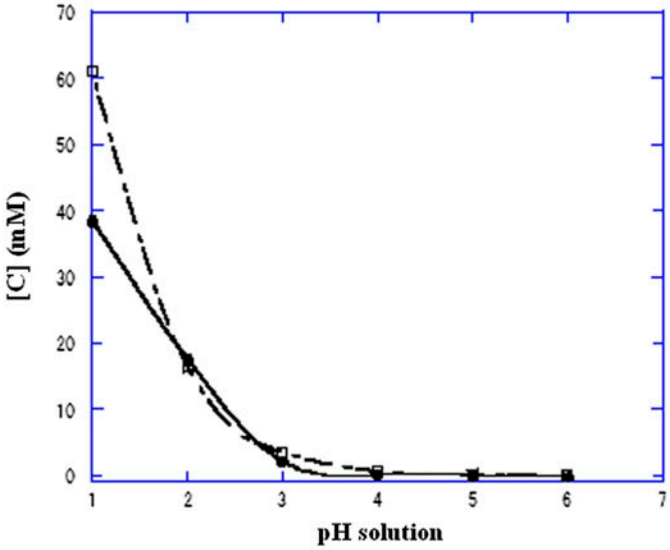

Figure 8. Determination of solubility of (●) [Co(2,2′-dpdtc)$_3$], (□) [Co(3,3′-dpdtc)$_3$] in pH 1–7.

4. Conclusion

The ligands, 2,2′-dpdtc and 3,3′-dpdtc can coordinate through two sulfurs and two picolyl nitrogens, but the present complexes have MS_6 coordination. These complexes are insoluble in water and alkaline solution, but act as indicators in acidic media due to the deeper color in acidic aqueous solution below pH 2. Further research should examine the polymerization with these complexes as starting materials and this, in particular, will reveal the difference of polymerization between 2,2′-dpdtc and 3,3′-dpdtc.

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