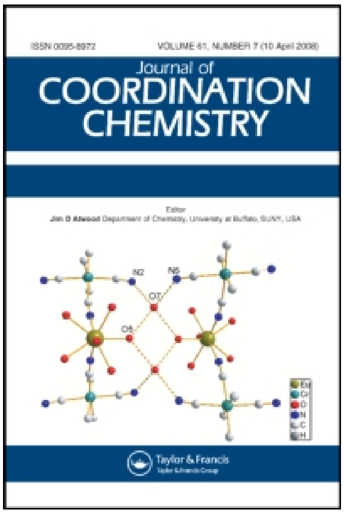

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Transition metal complexes of bidentate *p-tert*-butylcalix[4]arene *S*-alkyldithiocarbazate Schiff bases

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Transition metal complexes of bidentate *p-tert*-butylcalix[4]arene *S*-alkyldithiocarbazate Schiff bases

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The calix[4]arene-based podand, which incorporates two Schiff-base functions derived from *S*-alkyldithiocarbazate in 1,3-alternate positions on the lower rim has been prepared and reacted with transition metal ions. X-ray single crystal diffraction of nickel and copper complexes shows that two iminothiolate domains are monoanionic bidentate planar chelators to coordinate one metal in distorted tetrahedral geometry.

Keywords: Calixarene; Schiff base; salen; dithiocarbazate; metallic complex; crystal structure

1. Introduction

Calixarenes have structural and chemical diversity, allowing their use in synthesis of various molecular architectures [1]. Calixarenes have advantage over other members of the family due to features such as easy accessibility, well-defined structures, variable conformation, and easy modification [2]. Coordination chemistry of calixarenes has shown these compounds as selective binders, carriers, and also as building blocks for the construction of complexes [3, 4]. Calix[4]arenes are the lowest oligomers in the series, are readily available, and numerous metal complexes have been prepared and structurally authenticated. The rigid organic backbone of calix[4]arenes provides a platform for assembly of several metal centers in close proximity. The vast majority of these metallocalix[4]arene derivatives exist as either mono or binuclear complexes, retaining a cone-like conformation for the parent ligands. Recently metal complexes containing larger ring systems such as calix[6]arene and calix[8]arene have also attracted attention [5–7]. Schiff bases have been employed widely in the formation of metal complexes and in the study of inclusion phenomena, owing to their relatively easy preparation, remarkable stability, and high versatility. The fusion of the Schiff base and calixarene properties into a unique entity can give an interesting and versatile system with very peculiar coordination properties. Several reports have demonstrated the introduction of Schiff bases at the lower or upper rim of calixarenes and used them mostly as cation or anion receptors and carriers [8–12]. Although calixarene Schiff bases

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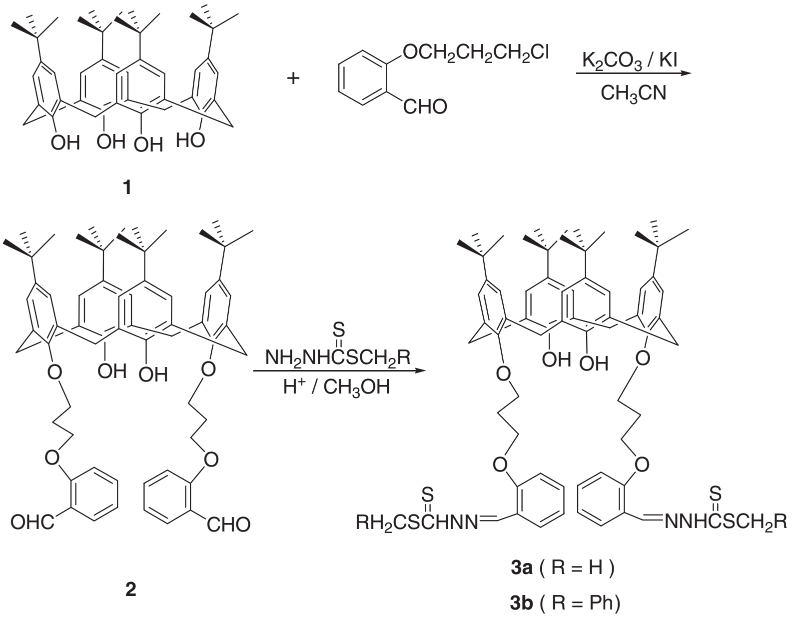
in ion recognition, extraction, and transportation have long been established, study of preparation and crystal structures of transition metal complexes of calixarene Schiff bases have not been investigated in detail.

Condensation products of carbonyl compounds with *S*-alkyldithiocarbazates are a special family of sulfur-containing Schiff bases [13–15]. Considerable attention continues to be given to these and related ligands and their metal complexes since some Schiff bases of this kind possess biochemical and pharmacological properties as therapeutic agents [16]. Apart from their biological activity, nitrogen–sulfur donor ligands of thiosemicarbazides and thiosemicarbazones and their metal complexes generate intriguing stereochemical, electrochemical, and electronic properties [17, 18]. To the best of our knowledge, the utilization of calixarenes bearing dithiocarbazate subunits at their lower rim have not been examined for coordination despite the availability of facile synthetic protocols. As part of an ongoing investigation of the coordination environment afforded by calixarenes [19], herein we report the preliminarily results of Schiff bases derived from *S*-alkyldithiocarbazate with calix[4]arene as platform for the construction of transition metal complexes.

2. Results and discussion

2.1. *Synthesis and characterizations*

Calix[4]arene Schiff bases were prepared in two steps by the reactions depicted in scheme 1. First, aldehyde functions were incorporated by *O*-alkylation on the lower rim of calix[4]arene according to a literature method [20, 21]. The reaction was carried



Scheme 1. Synthetic route of Schiff-base ligands **3a**–**3b**.

out by refluxing the mixture of *p*-*tert*-butylcalix[4]arene **1** with *O*-chloropropoxybenzaldehyde in $K_2CO_3/KI/CH_3CN$ for about 4 days. 1,3-Disubstituted **2** was obtained in good yield. Recently a report showed that this kind of calixarene aldehyde derivative can be prepared with an alternate route, in which the initially prepared 1,3-*bis*(bromopropyl)calix[4]arene was refluxed with *p*-hydroxybenzaldehyde in the system of K_2CO_3/CH_3CN [22]. Treating calixarene dialdehyde **2** with *S*-methyldithiocarbazate or *S*-benzyldithiocarbazate in methanol gave the Schiff bases **3a** and **3b** in moderate yields. Compounds **3a** and **3b** were characterized by IR and ^1H, ^{13}C NMR spectra. For example, the ^1H NMR spectrum of **3b** displays doublets at 3.34 and 4.24 for the methylene bridge protons. This typical AB pattern for the axial and equatorial protons indicated that ligand **3b** existed in symmetrical cone-conformation. This was confirmed by singlets at 1.01 and 1.28 ppm for the *t*-butyl protons in the ratio of 1 : 1. The NH protons, azo-methine (CH=N), and methylene in benzyl appeared as three singlets at 10.26, 8.21, and 4.51, respectively, showing the two podand arms are magnetically equivalent. The amino signal at 10.26 ppm also shows that the thioamide function –NH–C(=S)SR exists as the thione tautomer, not in thiol form, although an equilibrium mixture of the thione and thiol tautomeric forms may be expected to exist in solution. The IR spectra of **3a** and **3b** do not display a mercapto band at 2570 cm^{-1}, also indicating that in the solid state the Schiff base remains in the thione tautomer.

The complexation reactions were carried out by stirring methanol and chloroform solution of **3a** and **3b** with transition metal acetates at room temperature for 10 h. The resulting precipitates were collected and pure complexes were characterized by UV–Vis and IR spectroscopy (table 1) and confirmed by the X-ray single crystal diffraction.

2.2. *Crystal structure*

Single crystals of **3a**-Ni and **3b**-Cu were formed when a chloroform/methanol solution was allowed to slowly evaporate for a couple of weeks. The perspective views with atomic numbering are shown in figures 1 and 2. The crystal data and refinement details are given in table 2. The crystals have structural pattern similar to the calix[4]arene remaining in the cone-conformation. The two arms of Schiff base on the calixarene platform are in deprotonated thiolate form to coordinate to one metal, forming a metallic macrocycle framework. In **3a**-Ni the Ni^{2+} ion is coordinated through azomethine nitrogens N(1), N(3), and the mercapto-sulfurs S(2), S(3) to form a distorted square-planar geometry with N(1)–Ni–N(3), N(1)–Ni–S(3), N(3)–Ni–S(2), and S(2)–Ni–S(3) angles of 101.8(3)°, 86.7(2)°, 86.8(2)°, and 89.67(2)°. The C–N bond distances of the bi-chelated ligands C(52)–N(1), C(45)–N(3), C(53)–N(2), C(54)–N(4) range from 1.287(10)–1.298(11)A, typical for double bond Schiff-base compounds. The C–S bond distances of C(53)–S(3) 1.706(10) and C(54)–S(2) 1.738(11) Å indicate single bond character supporting that complex formation involves the ligand in its thiol form. The C(53)–S(1) 1.757(10) and C(54)–S(4) 1.747(10) Å are normal for C–S single bonds. The Ni(1)–N(1) and Ni(1)–N(3) bond lengths of 1.915(7) and 1.923(7) Å are shorter than that found in a nickel complex of benzyl *N*-[1-(thiophen-2yl)ethylidene]hydrazine carbodithioate reported recently (Ni–N 2.2673(3)) [18]. The Ni(1)–S(2) and Ni(1)–S(3) bond lengths of 2.140(3), 2.145(3) are also shorter than Ni–S bond length 2.4819(11) Å in that compound.

Table 1. The physical data of metal complexes.

Compound	Color	Yield (%)	m.p. (°C)	UV (nm)	IR (cm^{-1})
3a-Mn	Yellow	62	180–185	292, 329	3313, 2958, 2870, 1600, 1484, 1362, 1298, 1244, 1201, 1163, 1111, 1049, 1016, 952, 872, 753
3a-Co	Brown	87	229–235	281	3414, 2958, 2871, 1602, 1479, 1362, 1297, 1243, 1203, 1118, 1047, 952, 873, 755, 628
3c-Ni	Yellow	76	208–213	280, 332	3414, 2957, 2870, 1597, 1481, 1360, 1298, 1247, 1202, 1117, 1049, 1012, 950, 874, 752, 629
3a-Cu	Dark green	89	197–200	292, 350	3318, 2958, 2870, 1579, 1480, 1358, 1300, 1250, 1202, 1119, 1051, 1020, 950, 874, 753, 633
3a-Zn	Light yellow	85	230–235	291, 362	3313, 2958, 2870, 1600, 1484, 1362, 1298, 1244, 1201, 1163, 1111, 1049, 1016, 952, 872, 753
3b-Co	Brown	72	195–198	288	3412, 2958, 2870, 1597, 1479, 1393, 1360, 1298, 1202, 1118, 1050, 1017, 950, 874, 755, 701
3b-Ni	Yellow	71	204–208	282, 328	3324, 2958, 2871, 1596, 1483, 1360, 1297, 1248, 1202, 1118, 1050, 1002, 875, 754, 702
3b-Cu	Green	92	183–184	292, 357	3361, 2958, 2870, 1598, 1481, 1398, 1358, 1299, 1251, 1202, 1165, 1120, 1051, 1014, 957, 876, 755, 702, 636
3b-Zn	Light yellow	75	172–174	291, 368	3413, 2958, 2870, 1598, 1480, 1457, 1359, 1300, 1248, 1201, 1165, 1119, 1050, 1021, 953, 874, 755
3b-Cd	Light yellow	80	178–180	291, 359	3414, 2957, 2870, 1599, 1476, 1355, 1297, 1247, 1202, 1118, 1051, 1019, 944, 876, 754, 701, 629

In **3b**-Cu the calix[4]arene also exists in cone form, but the steric interaction of the two bulky bisphenol units causes the two bisphenol substituted aryl rings to be oriented perpendicular to the plane of the methylene bridge carbons. The other two aryl rings are inclined at an angle of 45°. The Cu^{2+} is a distorted tetrahedron with each iminothiolate of the Schiff base coordinated as a uninegative bidentate NS ligand via the azomethine nitrogen and the mercaptide sulfur. The Schiff base is singly deprotonated in the complex. This is accompanied by tautomerism to the iminothiolate with the negative charge (generated upon deprotonation) on the mercaptide sulphur atom delocalized in the C–N–N–C system as indicated by their intermediate bond distances: N(5)–N(6) = 1.423(10), N(5)–C(54) = 1.308(10), and N(6)–C(55) = 1.270(10). The C(55)–S(1) and C(62)–S(2) bonds of 2.226(3), 2.209(10) Å are essentially single bonds while the C–N and N–N bond orders are closer to two than one. The Cu(1)–S(1), Cu(1)–S(3) and Cu(1)–N(5), Cu(1)–N(7) distances compare well with those found in other copper(II) complexes of related sulfur-containing Schiff-base ligands [14, 15].

There are intermolecular interactions in the crystal, i.e. in **3a**-Ni the H21a, H56a, and H60b distances of methyl to benzene of salicylaldehyde unit is 2.346, 2.848, and 3.099 Å, respectively, which means relatively strong C–H $\cdots \pi$ interaction (figure 3). Through C21–H21a $\cdots \pi$ and C56–H56a $\cdots \pi$ interactions a double-stranded chain was

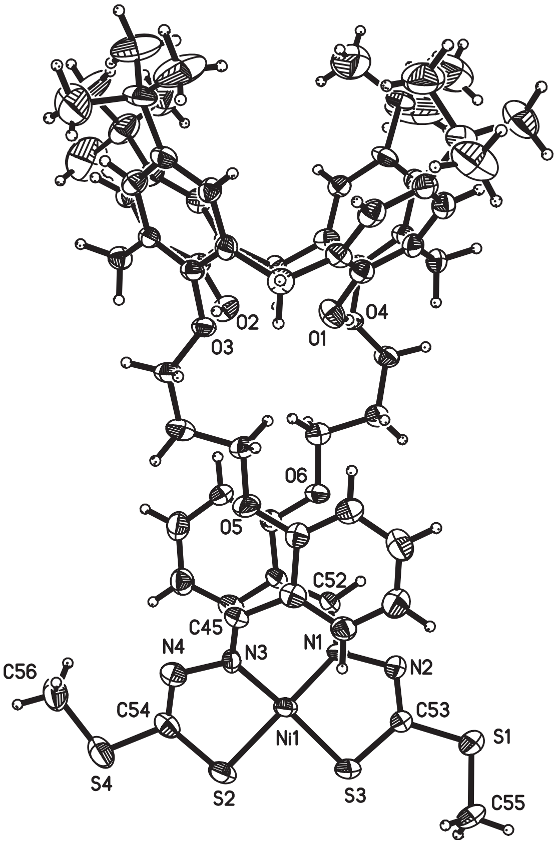


Figure 1. Crystal structure of **3a**-Ni.

formed and by interaction of C60–H60b $\cdots \pi$ linkage, a 2-D coordination layer was observed (figure 4).

3. Conclusions

The synthesis of calix[4]arene-based podand incorporating two Schiff-base functions derived from *S*-alkyldithiocarbazate in 1,3-alternate positions on the lower rim has been achieved. These ligands coordinated with transition metal ions to form complexes on the calixarene platform. X-ray single crystal diffraction of the nickel and copper complexes show that two iminothiolate domains in calix[4]arene are monoanionic bidentate planar chelators coordinating to one metal in distorted tetrahedral geometry.

4. Experimental

4.1. *Reagents and instruments*

All reagents and solvents were commercially available of analytical grade and used as received. Further purification and drying by standard methods were employed with

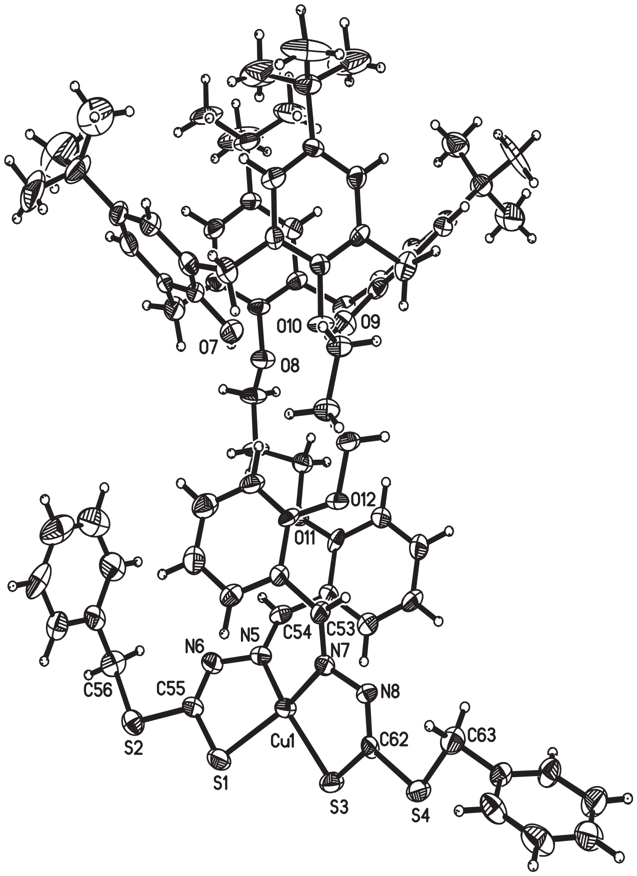


Figure 2. Crystal structure of **3b**-Cu.

distillation prior to use when necessary. *p*-*tert*-Butylcalix[4]arene [23], *O*-(3-chloropropoxy)benzaldehyde, *S*-methyl dithiocarbazate, and *S*-benzyldithiocarbazate were prepared by published methods. Melting points were taken on a hot-plate microscope apparatus and are uncorrected. ^{1}H NMR spectra were recorded with a Bruker AV-600 spectrophotometer (600 MHz for ^{1}H NMR). IR spectra were obtained on a Bruker Tensor27 spectrometer (KBr disc). X-ray data were collected on a Bruker Smart APEX-2 diffractometer.

4.2. *Synthesis of 5,11,17,23-tetra-p-tert-butyl-25,27-di(O-formylphenoxypropyl)-26,28-dihydroxycalix[4]arene (2)*

A suspension of **1** (8.0 mmol, 5.20 g) and anhydrous potassium carbonate (43.5 mmol, 6.0 g), potassium iodide (1.0 g, 6.0 mmol) in dry acetonitrile (150 mL) was refluxed under nitrogen for 2 hours. Then *O*-(3-chloropropoxy)benzaldehyde (18.0 mmol, 3.56 g) was added. The reaction mixture was refluxed for 4 days. After removal of most of the acetonitrile, the residue was put in water. The resulting precipitates were collected by filtration and recrystallized from a mixture of chloroform and ethanol to give **2**, light yellow solid, 7.20 g (92.6%). m.p. 100–108°C; ^{1}H NMR ($CDCl_3$, 600 Hz) δ: 10.50

Table 2. Crystal data and structure refinement details of the complexes.

	3a-Ni	**3b**-Cu
Empirical formula	$C_{73}H_{86}Cl_{15}N_4NiO_6S_4$	$C_{82}H_{92}Cl_6CuN_4O_6S_4$
Formula weight	1834.16	1636.08
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71070
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions (Å °)		
a	12.737(2)	12.048(2)
b	71.729(2)	92.356(3)
c	17.967(3)	13.905(3)
α	78.764(2)	95.129(3)
β	21.087(3)	26.652(5)
γ	86.660(2)	107.368(3)
Volume (Å^3)	4494.5(12)	4233.5(14)
Z	2	2
Calculated density (g cm^{-3})	1.355	1.284
Absorption coefficient (mm^{-1})	0.803	0.072
$F(000)$	1894	1714
θ range for data collection	1.8–25.5	1.5–25.5
hkl ranges	15–14, −21–21, −25–25	−14–14, −16–16, −32–28
Reflections collected/unique	34,313/16,602 [$R_{(int)} = 0.123$]	32,535/15,667 [$R_{(int)} = 0.228$]
Completeness to $\theta = 27.50$	99.2%	99.3%
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	16,602/20/952	15,667/18/937
Goodness-of-fit on F^2	0.931	0.896
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0864$, $wR_2 = 0.2084$	$R_1 = 0.0807$, $wR_2 = 0.1426$
R indices (all data)	$R_1 = 0.2880$, $wR_2 = 0.3200$	$R_1 = 0.3471$, $wR_2 = 0.2389$
Largest different peak and hole (e Å^{-3})	0.757 and −0.657	0.628 and −0.426

Note: Weighting scheme: $w = 1/[\sigma^2\,(F_o^2) + (0.1660P)^{\,2} + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3'$.

(s, 2H, CHO), 7.80 (br, 2H, ArH), 7.70 (s, 2H, ArOH), 7.53 (br, 2H, ArH), 7.08 (br, 2H, ArH), 7.06 (s, 4H, ArH), 7.00 (br, 2H, ArH), 6.87 (s, 4H, ArH), 4.52 (br, 4H, OCH_2), 4.24 (d, $J = 12.0$ Hz, 4H, $ArCH_2Ar$), 4.15 (br, 4H, OCH_2), 3.35 (d, $J = 12.0$ Hz, 4H, $ArCH_2Ar$), 2.42 (br, 4H, CH_2), 1.29 (s, 18H, $C(CH_3)_3$), 1.00 (s, 18H, $C(CH_3)_3$); IR (KBr) ν: 3406 (m), 2959 (vs), 2870 (m), 1689 (s), 1599 (s), 1483 (vs), 1390 (m), 1363 (w), 1292 (s), 1240 (s), 1199 (s), 1051 (s), 982 (w), 756 (m) cm^{-1}. Anal. Calcd for $C_{64}H_{76}O_8$: C, 78.98; H, 7.87. Found: C, 78.75; H, 8.23.

4.3. *Synthesis of 5,11,17,23-tetra-p-tert-butyl-25,27-di(o-S-methyldithiocarbazato-methylidene phenoxypropyl)-26,28-dihydroxycalix[4]arene (3a)*

To a 100 mL round-bottomed flask was added **2** (1.0 mmol, 0.972 g), *S*-methyldithiocarbazate (2.2 mmol, 0.27 g), and 50 mL of methanol as well as one drop of hydrochloric acid. The mixture was stirred at room temperature for 2 days. The resulting yellow precipitates were collected and recrystallized with chloroform/ethanol to give **3a**: yellow solid, 0.51 g (43%). m.p. 135 ~ 138°C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 10.26 (s, 2H, NH), 8.19 (s, 2H, CH=N), 7.89 (br, 2H, ArH), 7.86 (s, 2H, OH), 7.35 (br, 2H, ArH), 7.08 (s, 4H, ArH), 7.05 (s, 2H, ArH), 6.96 (br, 2H, ArH), 6.91 (s, 4H, ArH), 4.45 (br, 4H, OCH_2), 4.27 (d, $J = 12.0$ Hz, 4H, $ArCH_2Ar$), 4.13 (br, 4H, OCH_2), 3.37 (d, $J = 12.0$ Hz, 4H, $ArCH_2Ar$), 2.62 (s, 6H, SCH_3), 2.34 (br, 4H, CH_2), 1.28 (s, 18H,

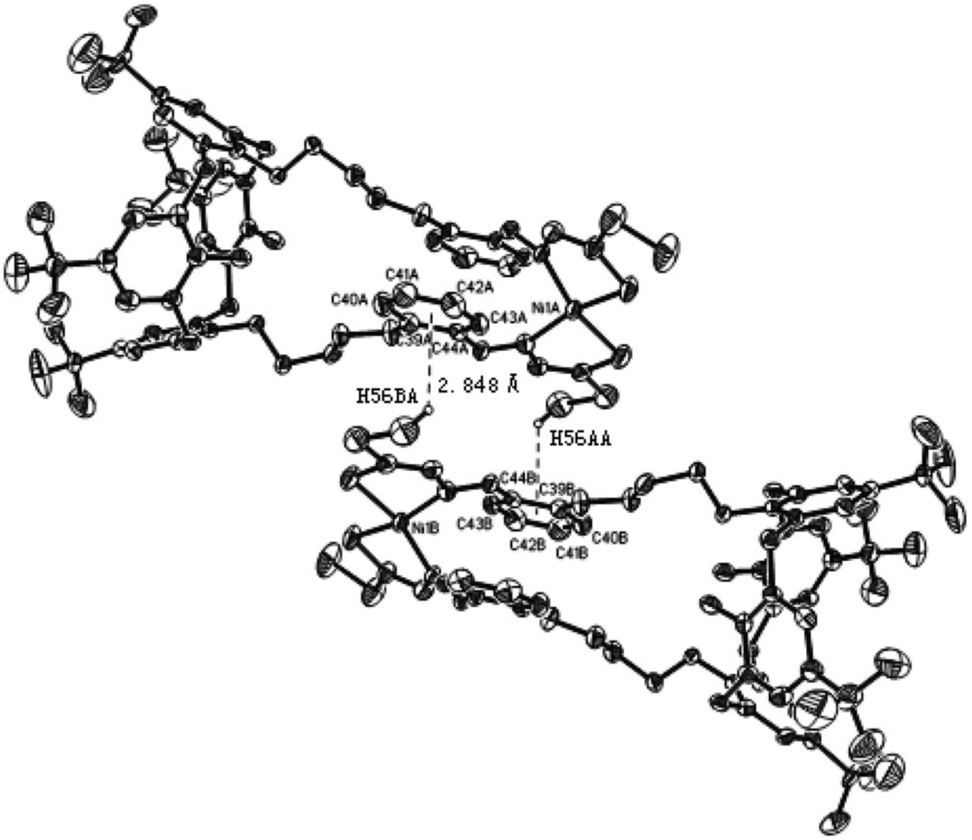


Figure 3. The C–H ··· interactions in **3a**-Ni.

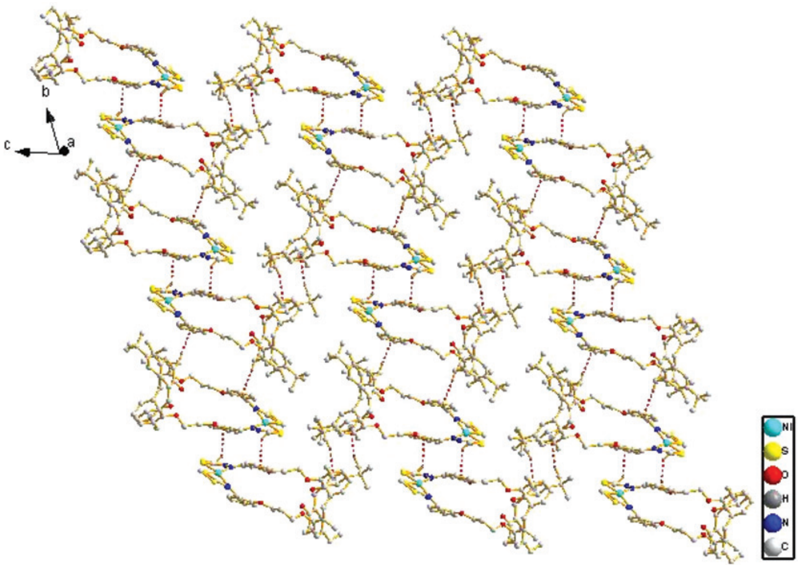


Figure 4. View of hydrogen-bonded layer of **3a**-Ni.

$C(CH_3)_3$), 1.06 (s, 18H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 600 MHz) δ: 199.8, 157.8, 150.3, 149.3, 147.7, 142.2, 141.5, 132.9, 132.4, 127.7, 126.7, 125.9, 125.8, 125.3, 121.5, 121.1, 112.2, 72.8, 65.5, 34.1, 33.9, 31.8, 31.7, 31.4, 31.1, 29.9; IR (KBr) ν: 3402 (w), 2958 (vs), 2870 (m), 1600 (m), 1482 (vs), 1360 (m), 1307 (s), 1249 (s), 1201 (s), 1097 (m), 1046 (s) cm^{-1}. Anal. Calcd for $C_{68}H_{84}N_4O_6S_4$: C, 69.12; H, 7.17; N, 4.74. Found: C, 68.75; H, 7.23; N, 4.58.

4.4. *Synthesis of 5,11,17,23-tetra-p-tert-butyl-25,27-di(o-S-benzyldithiocarbazato-methylidene phenoxypropyl)-26,28-dihydroxycalix[4]arene (3b)*

To a 100 mL round-bottomed flask was added **2** (1.0 mmol, 0.972 g), *S*-benzyldithiocarbazate (2.2 mmol, 0.44 g), and 50 mL of methanol as well as one drop of hydrochloric acid. The mixture was stirred at room temperature for 2 days. The resulting yellow precipitates were collected and recrystallized with chloroform/ethanol to give **3b**: 0.62 g (47%). m.p. 207–208°C; ^1H NMR ($CDCl_3$, 600 MHz) δ: 10.26 (s, 2H, NH), 8.21 (s, 2H, CH=N), 7.85 (d, $J = 7.2$ Hz, 2H, ArH), 7.80 (s, 2H, OH), 7.40, 7.39 (s, s, 4H, ArH), 7.28 ~ 7.30 (m, 6H, ArH), 7.07 (s, 4H, ArH), 7.05 (s, 2H, ArH), 6.95 (d, $J = 7.2$ Hz, 2H, ArH), 6.88 (s, 6H, ArH), 4.51 (s, 4H, SCH_2Ph), 4.43 (br, 4H, OCH_2), 4.23 (d, $J = 12.0$ Hz, 4H, $ArCH_2Ar$), 4.09 (br, 4H, OCH_2), 3.34 (d, $J = 12.0$ Hz, 4H, $ArCH_2Ar$), 2.33 (br, 4H, CH_2), 1.28 (s, 18H, $C(CH_3)_3$), 1.01 (s, 18H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 600 MHz) δ: 198.1, 157.8, 150.4, 149.3, 147.4, 146.7, 144.4, 141.5, 136.1, 132.7, 132.5, 129.5, 128.6, 127.4, 126.8, 125.9, 125.4, 121.4, 121.1, 112.2, 77.6, 65.4, 39.4, 34.1, 33.9, 31.7, 31.4, 31.1, 29.9; IR (KBr) ν: 3401 (m), 2957 (vs), 2870 (m), 1600 (s), 1481 (vs), 1307 (s), 1246 (s), 1201 (s), 817 (m), 754 (m), 704 (m) cm^{-1}. Anal. Calcd for $C_{80}H_{92}N_4O_6S_4$: C, 72.69; H, 6.95; N, 4.20. Found: C, 72.81; H, 7.14; N, 4.15.

4.5. *General procedure for the synthesis of transition metal complexes of (3a) and (3b)*

To a transition metal acetate (0.3 mmol) in methanol (15 mL) was added **3a** or **3b** (0.3 mmol) in chloroform (10 mL) and the solution was stirred at room temperature for about 2 days. The precipitate was filtered, washed with cold methanol, and dried in air to give the complexes. Metal ions used were manganese, cobalt, nickel, copper, and zinc.

Supplementary material

Single crystal X-ray diffraction data are deposited with CCDC (deposition numbers **3a**-Ni: CCDC 688285; **3b**-Cu: CCDC 688286).

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