Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Cobalt(III) Supramolecuar Complex: Synthesis, Crystal Structure and Anions Recognition Properties of 6,7-Dinitroquinoxaline-2,3-dione

Ming Yu[a]; Hai Lin[b]; Huakuan Lin[a]
[a] Department of Chemistry, Nankai University, Tianjin, China [b] State Key Laboratory of Functional Polymer Materials for Adsorption and Seperation, Nankai University, Tianjin, China

To cite this Article Yu, Ming , Lin, Hai and Lin, Huakuan(2008) 'Cobalt(III) Supramolecuar Complex: Synthesis, Crystal Structure and Anions Recognition Properties of 6,7-Dinitroquinoxaline-2,3-dione', Supramolecular Chemistry, 20: 3, 309 — 315

To link to this Article: DOI: 10.1080/10610270701258659

URL: http://dx.doi.org/10.1080/10610270701258659

Supramolecular Chemistry, April–May 2008 VOL. 20 (3), pp. 309–315

Cobalt(III) Supramolecuar Complex: Synthesis, Crystal Structure and Anions Recognition Properties of 6,7-Dinitroquinoxaline-2,3-dione

MING YU[a], HAI LIN[b] and HUAKUAN LIN[a,*]

[a]*Department of Chemistry, Nankai University, Tianjin 300071, China;* [b]*State Key Laboratory of Functional Polymer Materials for Adsorption and Seperation, Nankai University, Tianjin 300071, China*

(Received 10 January 2007; Accepted 3 February 2007)

A 3D supramolecular complex $[Co(III)(Phen)_2Cl_2][DNQ]Cl{\cdot}H_2O$ (DNQ = 6,7-dinitroquinoxaline-2,3-dione) has been synthesized and determined by single-crystal X-ray analysis. Anion binding studies carried out using ^1H NMR and UV-visible revealed that a genuine hydrogen bond interaction between anion receptor 2 and Cl^- can be detected, but fluoride is deprotonating the anion receptor 2. X-ray analysis results show that it is not possible for the two amide nitrogen atoms of anion receptor to form hydrogen bonds to a chloride ion in the presence of small aliquots of water.

Keywords: Supramolecular complex; Hydrogen bond; Crystal structure; Anion recognition

INTRODUCTION

Anions are ubiquitous throughout biological systems; it is believed that they carry genetic information (DNA is a polyanion) and participate in 70% of all enzymatic reactions [1–5]. More recent developments include exciting advances in anion-templated syntheses and directed self-assembly, ion-pair recognition, and the function of anions in supramolecular catalysis [6–9]. Taking into account the crucial importance of hydrogen bonding to the anion recognition process for anion receptors, the design of the target receptors linking two subunits: amide (CONH) groups and nitro groups subunits into the aromatic ring. It is related to and builds upon the earlier work of Sessler and co-workers [10], in which they study anion recognition properties of the fused dipyrrolylquinoxaline phenanthroline derivative, and its ruthenium (II) and cobalt (III) complexes. The latter species, containing as they do electron withdrawing metal centers, show the best selectivity for F^- over other halide anions. In this work, our intent was to prepare the previously unreported $[Co(Phen)_2(DNQ)]^{3+}$ (DNQ = 6,7-dinitroquinoxaline-2,3-dione) and investigate its anion recognition properties, but surprisingly the supramolecular complex $[Co(Phen)_2Cl_2][DNQ]Cl{\cdot}H_2O$ formed instead. The synthesis, properties, and single-crystal X-ray structure of $[Co(Phen)_2Cl_2][DNQ]Cl{\cdot}H_2O$ (**3**) are reported (Scheme 1).

EXPERIMENTAL

Reagents

All anions, in the form of tetrabutylammonium salts, were purchased from Sigma-Aldrich Chemical Co., stored in a desiccator under vacuum containing self-indicating silica, and used without any further purification. Solvents were purified prior to use and stored under nitrogen. Dimethyl sulfoxide was dried with calcium hydride and distilled at reduced pressure prior to use. Unless stated otherwise, commercial grade chemicals were used without further purification.

Synthesis

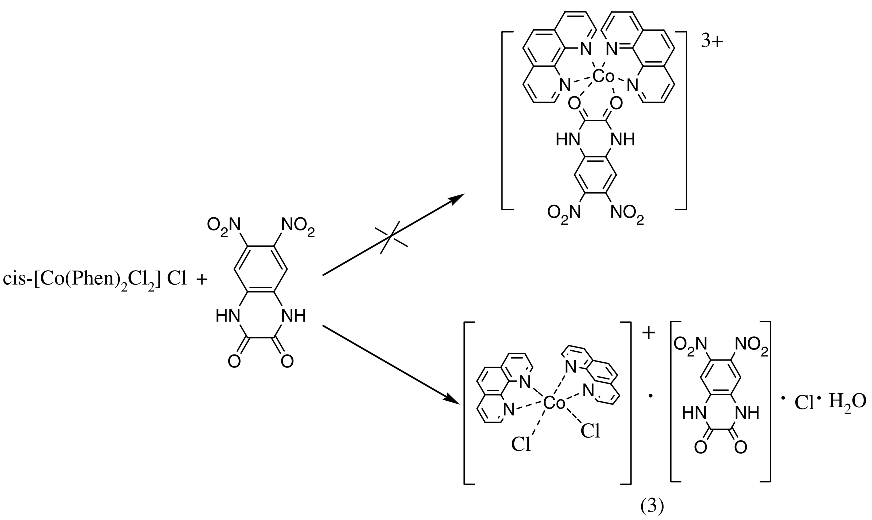
4,5-Dinitro-o-phenylenediamine (1)

4,5-Dinitro-o-phenylenediamine was synthesized according to methods described in the literature

---

*Corresponding author. Tel.: + 86-22-23502624. Fax: + 86-22-23502458. E-mail: hklin@nankai.edu.cn

ISSN 1061-0278 print/ISSN 1029-0478 online © 2008 Taylor & Francis
DOI: 10.1080/10610270701258659



SCHEME 1 The synthesis of $[Co(Phen)_2Cl_2][DNQ]Cl{\cdot}H_2O$ (**3**).

[11]. ^{1}H NMR (400 MHz, DMSO-d_6): 7.075 (S, 2H), 6.113 (S, 4H), Anal. Calcd. for $C_6H_6N_4O_4$: C 36.4%, H 3.0%, N 28.3%, Found, C 36.0%, H 3.1%, N 28.2%.

6,7-Dinitroquinoxaline-2,3-dione (2)

A mixture of 4,5-dinitro-o-phenylenediamine (1.0 g) and diethyl oxalate (15 ml) was heated under reflux for 12 h and then cooled. The precipitate of 6,7-dinitroquinoxaline-2,3-dione was filtered off and washed with 95% ethanol. ^{1}H NMR (400 MHz, DMSO-d_6): 7.870 (S, 2H), 12.523 (S, 2H), Anal. Calcd. for $C_8H_4N_4O_6$, C 38.1%, H 1.6%, N 22.2%, Found, C 37.9%, H 1.7%, N 22.0%.

Co(Phen)$_2$Cl$_2$][6,7-dinitroquinoxaline-2,3-dione]Cl·H$_2$O (3)

0.253 g (1 mmol) 6,7-dinitroquinoxaline-2,3-dione was dissolved in DMF solution (30 ml), then 0.565 g (1 mmol) *cis*-$[Co(Phen)_2Cl_2]Cl{\cdot}3H_2O$, which was synthesized by the published method [12], was added, the mixture was stirred for 12 h at room temperature, and the reaction solution turned deep green. Supramolecular complex [Co (Phen)$_2$Cl$_2$][6,7-dinitroquinoxaline-2,3-dione]Cl·H$_2$O were obtained after slow evaporation of a DMF solvent of over a period of three weeks.

Physical Measurements

Unless otherwise specified, all of the experiments were carried out at 298 ± 1 K. The ^{1}H NMR spectra were recorded on a Varian UNITY-plus 400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. UV-visible spectra were recorded on a Shimadzu UV-2450 PC spectrophotometer.

Absorption Titration Studies

The binding ability of anion receptor **2** for halide anions (as tetrabutylammonium salts) was investigated by UV–visible spectroscopy in DMSO solution using a constant host concentration (5.0×10^{-5} M) and increasing concentrations of anions (1–100 equiv). The changes in absorbance at 462 nm for anion receptor **2** was plotted against anion concentration and fitted by the equation as described by Connors [13].

^{1}H NMR Titrations

Anion receptor **2** (1.0×10^{-2} M in DMSO-d_6) was titrated against X^- (tetrabutylammonium salts) by incremental additions of a concentrated solution of the anion in DMSO-d_6.

Determination and Refinement of the Structure

The crystal structure was put on a bruker Smart 1000 diffractometer equipped with a graphitemonochromated Mo K_α radiation ($\lambda = 0.71073$ Å). Data were processed by using Bruker SMART system software and the Bruker SAINT program for integration of data frames. The data were corrected of absorption by means of the program SADABS. All subsequent computations were performed by using the SHELXTL program suite. The structure was solved by direct methods and refined by full-matrix least-squares methods. Hydrogen atoms were included in the structural model at calculated positions.

TABLE I Log K for receptors 2 interaction with anions

Species	F^-	Cl^-	Br^-	I^-	OH^-
Receptors 2	2.64 ± 0.10(**Log K_d**)	< 1 (**Log K_a**)	†	†	2.70 ± 0.10(**Log K_d**)

† Changes in the UV–visible spectra were not observed.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 624120.

RESULTS AND DISCUSSION

Anion Sensing

The interaction of anion receptor **2** with anions was investigated through UV–visible titrations by adding a standard solution of the tetrabutylammonium salt of anions to a dry DMSO solution of anion receptor **2** (Table I). Figure 1 shows the UV–visible spectra changes of anion receptor **2** during the titration with anions. Addition of F^- induces the formation of a new red-shifted absorption band at 462 nm with the decrease of the band at 340 nm. This new band matches well with the absorption band formed in tetrabutyl ammonium hydroxide, so it derives from the deprotonated anion species [14]. ^1H NMR was used to investigate the nature of anion coordination, and experiments were carried out in DMSO-d_6 (Fig. 3). Upon addition of 0.5 molar equiv of F^-, the majority of signals on the phenyl ring shift distinctly upfield owing to charge delocalization on the entire conjugated system with the deprotonation of anion receptor **2**, and the signal for the amide NH proton cannot be detected at this time. With increasing F^-, the phenyl signal shift upfield further, and these shifts stop after the addition of F^- up to 1 molar equiv. The stoichiometry between host and guest was determined by UV–visible Job plot, giving the receptor/fluoride stoichiometry of 1:1 (Fig. 2). So this deprotonation process can be expressed by the following Brönsted acid–base reaction equilibrium (Eq. (1))

$$LH + F^- \overset{Kd}{\rightleftharpoons} L^- + FH \qquad (1)$$

$$LH + Cl^- \overset{Ka}{\rightleftharpoons} [LH\ldots Cl]^- \qquad (2)$$

On the other hand, though Cl^- cannot induce distinctly spectral change in absorbance (Fig. 1), a genuine hydrogen bond interaction (Eq. (2)) between anion receptor **2** and Cl^- can be detected from the ^1H NMR titration spectra (Fig. 4). The signal ascribable to the NH proton of anion receptor **2** (12.50 ppm) is strengthened, and the phenyl signal shift downfield. This result indicates that a hydrogen bond complex between anion receptor **2** and the chloride ion is formed. The chloride ion forms hydrogen bonds to amide N—H moieties and aromatic C—H moieties of receptor **2**. The two hydrogen-bonds can also be seen in the crystal structure.

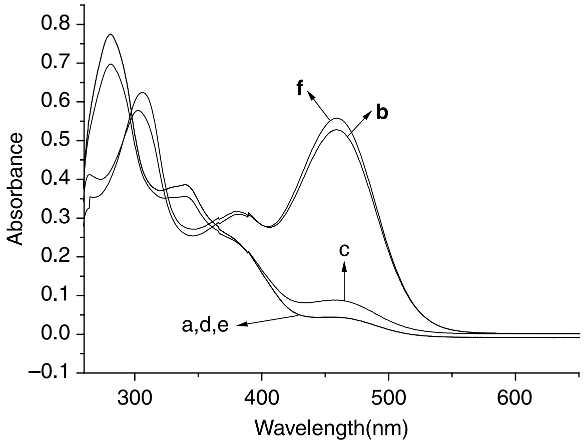


FIGURE 1 UV–vis spectral changes of anion receptor upon the addition of halide ions; (a) [anion receptor **2**] = 5.0 × 10^{-5} M; [**2**]:[X^-] = 1:100 equiv; (b) [F^-], (c) [Cl^-], (d) [Br^-], (e) [I^-], (f) [OH^-], DMSO, 25°C.

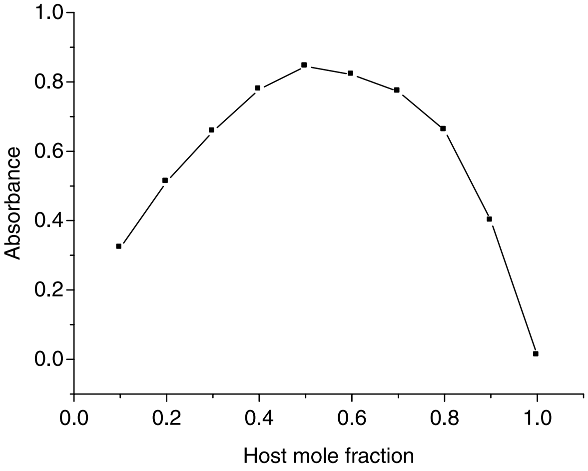


FIGURE 2 A Job plot of anion receptor **2** with tetrabutylammonium fluoride.

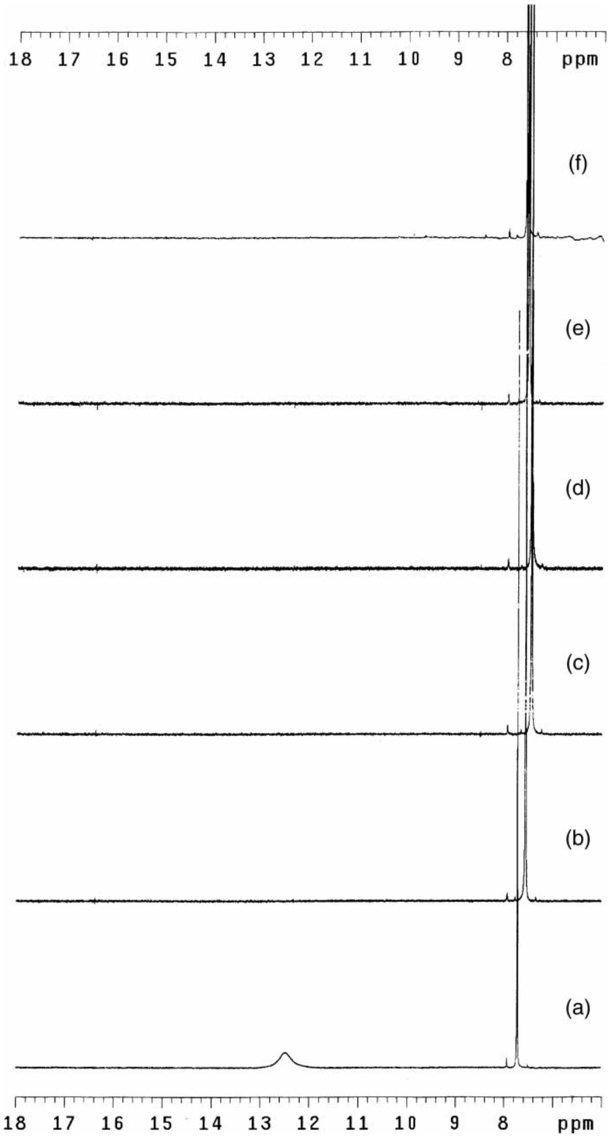


FIGURE 3 ^{1}H NMR(400 MHz) spectra of anion receptor **2** (1.0×10^{-2} M) in DMSO-d_6 in the absence (a) of and the presence of 0.5 (b), 1.0 (c), 2.0 (d), 3.0 (e), and 5.0 (f) equiv. of $[(Bu)_4N]F$.

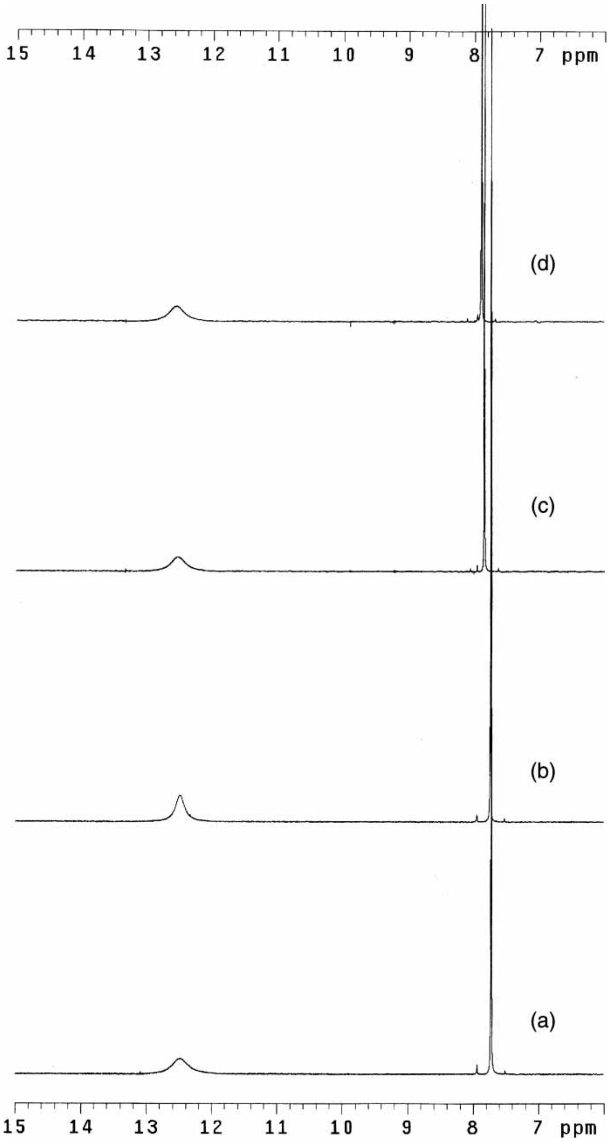


FIGURE 4 ^{1}H NMR(400 MHz) spectra of anion receptor **2** (1.0×10^{-2} M) in DMSO-d_6 in the absence (a) of and the presence of 0.5 (b), 1.0 (c), and 2.0 (d) equiv. of $[(Bu)_4N]Cl$.

Solid State Structures of 3

Slow evaporation of a DMF solution of **3** gave deep green crystals suitable for an X-ray structural determination. The crystallographic data are summarized in Table II. A view of the structure is shown in Fig. 5. The solid-state structure of **3** comprises cis-$[Co(Phen)_2Cl_2]^+$ cation, anion receptor **2**, chloride ion and water molecule in each asymmetric unit, which are linked through hydrogen bonds. The overall coordination environment of the Co (III) atom involves four nitrogen atoms of phenanthroline and two chloride atoms. Four of the Co—N bonds are relatively short (bond lengths 1.923 Å, 1.928 Å, 1.939 Å and 1.949 Å); the other two of Co—Cl contacts are significantly longer (bond lengths 2.227 Å and 2.228 Å), and they constitute a distorted octahedral geometry around the Co (III) atom (see Table III). The average bond distances of Co-N coincide with the values observed in $[Co(Phen)_2(CO_3)]^+$[15]. The bite angles between the phenanthroline chelate rings and cobalt atoms are 84.51° [N1—Co1—N2] and 84.09° [N4—Co1—N3] in good agreement with those reported for $[Co(Phen)(L\text{-}proline)_2]^+$[16]. Both of the coordinated chloride ions form hydrogen bonds to C—H moieties of another coordinated phenanthroline [C20 ($-$x, 1 $-$ y, 1 $-$ z) —H20...Cl1, C22 ($-$x, 2 $-$ y, 1 $-$ z) —H22...Cl2]. The 2D sheet complex synthon is formed by cis-$[Co(Phen)_2Cl_2]^+$ cation with hydrogen bonds and the intersheet space is filled with anion receptor **2**. The anion receptor **2** ties the sheet together with strong hydrogen bonding from the anion receptor **2**, to the hydrogen atoms of coordinated phenanthroline (C5—H5...O3,

TABLE II Crystal data and structure refinement details for (**3**)

	3
Empirical formula	$C_{32}H_{22}Cl_3CoN_8O_7$
Formula weight	795.86
Temperature (K)	294 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions:*a* (Å)	8.126(3)
b (Å)	10.093(4)
c (Å)	19.651(7)
α (deg)	93.671(6)
β (deg)	99.234(6)
γ (deg)	92.241(6)
Volume (Å^3)	1585.5
Z	2
Density (calculated) Mg/m^3	1.67
Absorption coefficient (mm^{-1})	0.859
F (000)	808
Crystal size (mm)	0.22 × 0.20 × 0.12
θ range for data collection (deg)	1.0 − 25.0
Index ranges	$-9 \leq h \leq 6$ $-12 \leq k \leq 11$ $-22 \leq l \leq 23$
Reflections collected	8118
Independent reflections[R(int)]	5566
Weighting scheme (*a, b*)†	0.1551,0.0000
Data/restraints/parameters	5566/3/460
Goodness-of-fit on F^2	1.040
Final R indices [I (2σ (I)]	$R_1 = 0.0738$ $wR_2 = 0.2114$
R indices (all data)	$R_1 = 0.1243$ $wR_2 = 0.2550$
Largest diff peak and hole (e·Å^{-3})	0.994 and − 1.089

†Weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$, where $P = (F_o^2 + 2F_c^2)/3$.

TABLE III Selected bond distances and angles

Bond	Angle (°)	Bond	Distance (Å)
N4—Co1—N1	176.21(2)	Co1—N4	1.923(5)
N4—Co1—N3	84.09(2)	Co1—N1	1.928(5)
N4—Co1—N2	92.51(2)	Co1—N3	1.939(6)
N4—Co1—Cl2	94.61(18)	Co1—N2	1.949(5)
N4—Co1—Cl1	88.77(18)	Co1—Cl2	2.227(2)
N1—Co1—N3	93.50(2)	Co1—Cl1	2.228(2)
N1—Co1—N2	84.51(2)		
N1—Co1—Cl2	87.66(16)		
N1—Co1—Cl1	94.14(17)		
N3—Co1—N2	89.14(2)		
N3—Co1—Cl2	177.06(16)		
N3—Co1—Cl1	89.37(16)		
N2—Co1—Cl2	88.27(16)		
N2—Co1—Cl1	177.93(16)		
Cl2—Co1—Cl1	93.25(7)		

C9—H9...O2, C14—H14...O1) (see Fig. 6). Aromatic π−π stacking arrangement in a face-to-face manner is observed between the anion receptor **2**. The chloride ion (Cl3) acting as the counter-ion is our target anion, which form strong hydrogen bonds to the N—H group of anion receptor **2**. The chloride ion forms hydrogen bonds to N5 (amide N—H moieties of receptor **2**), C29 (aromatic C—H moieties of receptor **2**), and O7 (H_2O molecular) with distances of 3.105 Å, 3.400 Å, and 2.992 Å, not to N6 (amide N—H moieties of receptor **2**). This result indicates that it is not possible for the two amide nitrogen atoms to form hydrogen bonds to a chloride ion in the presence of small aliquots of water. Thus, the water molecularly connects to chloride ion (Cl3) and amide nitrogen atom (N6) through hydrogen bonds forming a V-shaped structure. In addition, the water molecule is not coordinated to the cobalt atom (Table IV).

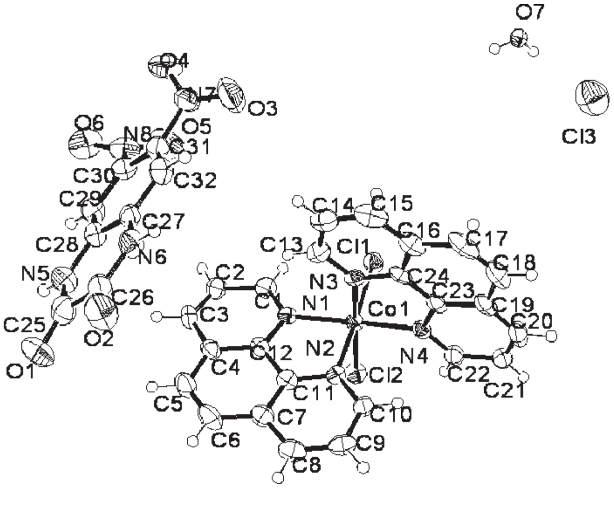


FIGURE 5 The structure of **3** with ellipsoids at 50% probability. The hydrogen atoms are shown as small circles with arbitrary radii.

CONCLUSIONS

In conclusion, a 3D supramolecular complex [Co(Phen)$_2$Cl$_2$][DNQ]Cl·H_2O has been determined by single-crystal X-ray analysis. The solid-state structure of **3** comprises cis-[Co(Phen)$_2$Cl$_2$]$^+$ cation, anion receptor **2**, chloride ion and water molecule in each asymmetric unit, which are linked through hydrogen bonds. Aromatic π−π stacking arrangement in a face-to-face manner is observed between anion receptors. The chloride ion as target anion forms hydrogen bonds to N5 (amide N—H moieties of receptor **2**), not to N6 (amide N—H moieties of receptor **2**). This result indicates that it is not possible for the two amide nitrogen atoms to form hydrogen bonds to a chloride ion in the presence of small aliquots of water. Moreover, fluoride is deprotonating the anion receptor **2**.

Supplementary Material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 624120.

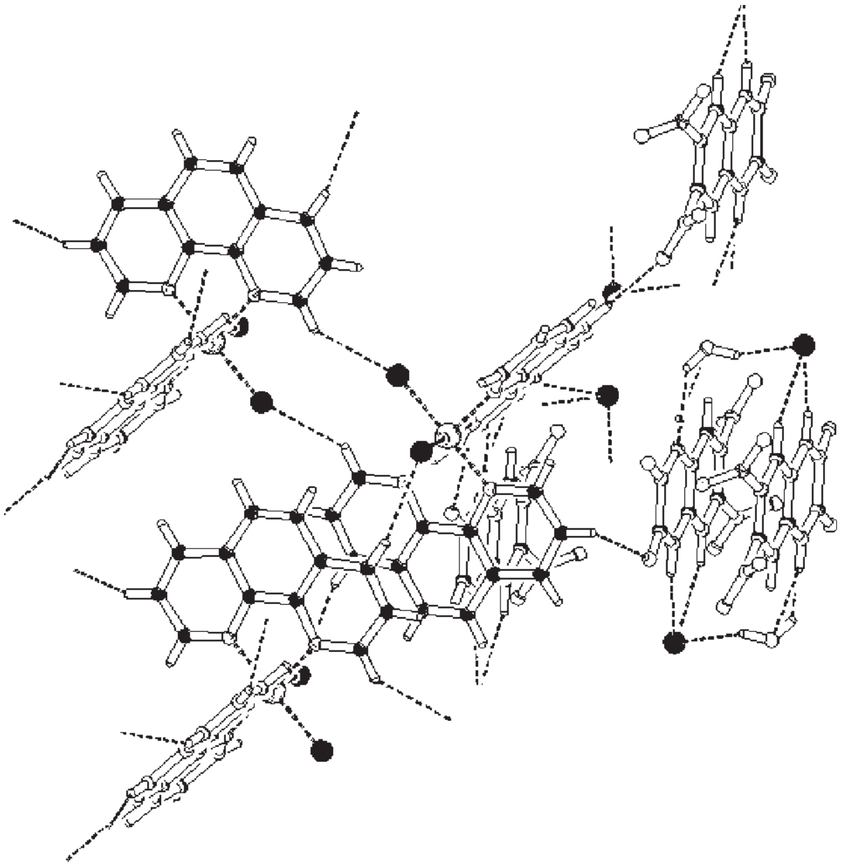


FIGURE 6 View of $[\mathrm{Co(Phen)_2Cl_2}]^+$ cation with an associated anion receptor, chloride ion and H_2O. Hydrogen bonds are shown as dotted lines.

TABLE IV Details of intermolecular hydrogen bonds in **3**

Donor—H... Acceptor	[ARU]	D—H	H...A	D...A	D—H...A
N5—H5...Cl3	1 − x, 1 − y, −z	0.8595	2.2737	3.105	162.63
N6—H6...O7	1 − x, 1 − y, −z	0.8599	2.1955	3.028	162.97
O7—H7A...N6	1 − x, 1 − y, −z	0.8296	2.4439	3.028	128.23
O7—H7B...Cl3	1 − x, 1 − y, −z	0.8318	2.2708	2.992	145.19
C5—H5...O3	x, 1 + y, z	0.9294	2.5160	3.353	149.89
C6—H6...Cl3	x, 1 + y, z	0.9298	2.6577	3.561	163.95
C8—H8...Cl3	−x, 1 − y, −z	0.9300	2.7387	3.531	143.70
C9—H9...O2	−x, 1 − y, −z	0.9304	2.5586	3.345	142.5
C10—H10...N4		0.9302	2.5565	3.025	111.56
C13—H13...N1		0.9305	2.5841	3.059	112.19
C14—H14...O1	1 − x, 1 − y, −z	0.9304	2.5316	2.994	111.02
C20—H20...Cl1	−x, 1 − y, 1 − z	0.9297	2.8115	3.623	146.52
C22—H22...Cl2	−x, 2 − y, 1 − z	0.9305	2.7190	3.516	144.21
C29—H29...Cl3	−x, 1 − y, −z	0.9300	2.6253	3.400	141.16

Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20371028, 20671052) and by the Natural Science Foundation of Tianjin (023605811).

References

[1] Beer, P. D.; Gale, P. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 486.

[2] Martínez-Máñez, R.; Sancenón, F. *Chem., Rev.* **2003**, *103*, 4419.

[3] Fabbrizzi, L.; Licchelli, M.; Rabaioli, G.; Taglietti, A. *Coord. Chem. Rev.* **2000**, *205*, 85.

[4] Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609.

[5] Christianson, D. W.; Lipscomb, W. N. *Acc. Chem. Res.* **1989**, *22*, 62.

[6] Lavigene, J. J.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3666.

[7] Gale, P. A.; Twyman, L. J.; Handlin, C. I.; Sessler, J. L. *Chem. Commun.* **1999**, 1851.

[8] Black, C. B.; Andrioletti, B.; Try, A. C.; Ruiperez, C.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 10438.

[9] Anzenbacher, Jr., P.; Jursíková, K.; Sessler, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 9350.

[10] Mizuno, T.; Wei, W. H.; Eller, L. R.; Sessler, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 1134.

[11] Cheeseman, G. W. H. *J. Chem. Soc.* **1962**, *84*, 1170.

[12] Grassini-Strazza, G.; Isola, S. *J. Chromatogr.* **1978**, *154*, 127.

[13] Connors, K. A. *Binding Constants: the Measurement of Molecular Complex Stability*;, 1st ed. John Wiley & Sons: New York, 1987.

[14] Wu, Y. K.; Peng, X. J.; Fan, J. L.; Gao, S.; Tian, M. Z.; Zhao, J. Z.; Sun, S. G. *J. Org. Chem.* **2006**, DOI: 10.1021/jo061634c.

[15] Niederhoffer, E. C.; Martell, A. E.; Rudolf, P.; Clearfield, A. *Inorg. Chem.* **1982**, *21*, 3736.

[16] Ye, B. H.; Zeng, T. X.; Han, P.; Ji, L. N. *Transition Met. Chem.* **1993**, *18*, 515.