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STRUCTURE OF A NEW SCHIFF BASE COBALT(III) COMPLEX WITH ANTIBACTERIAL ACTIVITY

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A new Schiff base cobalt(III) complex with the formula $[CoL^1L^2(N_3)]\cdot NO_3$ (L^1 is 2-[1-(2-phenylaminoethylimino)ethyl]phenolate, L^2 is N-phenylethane-1,2-diamine) is prepared and characterized by physicochemical methods and single crystal X-ray determination. The complex crystallizes in the triclinic system space group *P*-1, with $a = 8.504(2)$ Å, $b = 14.973(3)$ Å, $c = 20.676(4)$ Å, $\alpha = 100.021(3)°$, $\beta = 90.005(3)°$, $\gamma = 103.084(2)°$, $V = 2523.0(9)$ Å^3, $Z = 4$, $R_1 = 0.0732$, and $wR_2 = 0.1182$. Single crystal X-ray diffraction analysis reveals that the complex contains two mononuclear $[CoL^1L^2(N_3)]^+$ cations and two nitrate anions. The Co atom is six-coordinated in an octahedral geometry. The ligands and the cobalt(III) complex are screened *in vitro* for their antibacterial activity against *Bacillus subtillis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas aereuginosa*.

K e y w o r d s: Schiff base, cobalt(III) complex, synthesis, crystal structure, biological activity.

In the last few decades, considerable attention has been focused on Schiff bases and their complexes in the fields of coordination chemistry and biological chemistry [1—3]. Some Schiff bases were reported to possess antibacterial, antifungal, and antitumor activities [4—6]. Schiff base complexes have also been used as drugs. Moreover, it is well known that some drug activities, when administered as metal complexes, are being increased [7]. This work deals with the synthesis and characterization of a new cobalt(III) complex of $[CoL^1L^2(N_3)]\cdot NO_3$, where L^1 is 2-[1-(2-phenylaminoethylimino)ethyl]phenolate and L^2 is N-phenylethane-1,2-diamine. The coordination behavior of the ligands toward the cobalt(III) ion was investigated by IR, molar conductivity, and single crystal X-ray determination. The antibacterial activity of the ligands and the cobalt(III) complex was studied against the bacterial species *Bacillus subtillis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas aereuginosa*.

EXPERIMENTAL

Materials and methods. 2-Acetylphenol and N-phenylethane-1,2-diamine with analytical grade were available from Alfa Aesar Company. Cobalt nitrate and other chemicals with analytical grade were purchased from Beijing Chemical Reagent Company and were used without further purification. Carbon, hydrogen, and nitrogen were determined on a Perkin-Elmer 240C microanalyzer. The metal content was determined by complexometric titration with EDTA. IR spectra (4000—400 cm^{-1}), as KBr pellets, were recorded on a Nicolet FT-IR 170X spectrophotometer. Conductance measurement was carried out at room temperature on a freshly prepared 10^{-3} M methanol solution using a DDS-11A conductivity meter.

Synthesis of HL^1. A mixture of 2-acetylphenol (1.36 g, 10 mmol) and N-phenylethane-1,2-diamine (1.36 g, 10 mmol) in methanol (50 ml) was refluxed for 30 min. Then the solvent was evaporated to give yellow gummy product of HL^1 with quantitative yield. Analysis: Calcd. (%) for $C_{16}H_{18}N_2O$: C, 75.6; H, 7.1; N, 11.0. Found (%): C, 75.3; H, 7.2; N, 11.1.

Synthesis of $[CoL^1L^2(N_3)]\cdot NO_3$. 2-Acetylphenol (0.136 g, 1 mmol) and N-phenylethane-1,2-diamine (0.272 g, 2 mmol) were mixed in methanol (20 ml). To the mixture a methanolic solution (10 ml) of cobalt nitrate (0.291 g, 1 mmol) and sodium azide (0.065 g, 1 mmol) were added with stirring. The mixture was then stirred at room temperature for 2 h. The insoluble impurities were removed by filtration. Block red crystals, suitable for single crystal X-ray diffraction, were formed by slow evaporation of the filtrate in air for a few days. Yield: 73 %. Analysis: Calcd. (%) for $C_{24}H_{29}CoN_8O_4$: C, 52.2; H, 5.3; N, 20.3; Co, 10.7. Found (%): C, 51.9; H, 5.5; N, 20.1; Co, 11.0.

X-ray crystallography. The single crystal of the complex suitable for X-ray diffraction was mounted on a thin-walled glass fiber and aligned on the Bruker SMART 1000 CCD area diffractometer (graphite-monochromated MoK_α radiation, $\lambda = 0.71073$ Å). The θ range for data collection was 2.23—28.25° for the complex. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by least-square cycles. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to the secondary amines were located from a difference Fourier map and refined isotropically, with N—H distances restrained to 0.90(1) Å. The remaining hydrogen atoms were located as riding atoms and not refined. All calculations were performed using SHELXTL97 [8]. The data collection and refinement parameters are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Crystallographic data for the complex has been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 808163. This information may be obtained free of charge from: the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; website: http://www.ccdc.cam.ac.uk).

Microbiological test. For the microbiological test the filter paper disc method was applied according to the method reported by Gupta and co-workers [9]. The investigated isolates of bacteria were seeded in tubes with nutrient broth. The seeded nutrient broth (1 cm^3) was homogenized in the tubes with 9 cm^3 of melted (45 °C) nutrient agar. The homogeneous suspensions were poured into Petri dishes. The discs of filter paper (diameter 4 mm) were ranged on the cool medium. After cooling on the formed solid medium, 2×10^{-5} dm^3 of the investigated compounds were applied using a micro-

Table 1

Crystal data and refinement parameters for the complex

Chemical formula	$C_{24}H_{29}CoN_8O_4$	D_c, g/cm^3	1.454
M	552.5	μ(MoK_α), cm^{-1}	0.728
T, K	298(2)	F(000)	1152
Crystal shape / color	Block / red	Index ranges (h, k, l)	–8/10, –19/18, –26/24
Crystal size, mm	0.27×0.23×0.22	Independent reflections	10495
Crystal system	Triclinic	Observed reflections [$I \geq 2\sigma(I)$]	5508
Space group	P-1	T(min) / T(max)	0.8277 / 0.8563
a, b, c, Å	8.504(2), 14.973(3), 20.676(4)	Data / restraints / parameters	10495 / 4 / 681
α, β, γ, deg.	100.021(3), 90.005(3), 103.084(2)	Goodness of fit on F^2	1.020
		R_1, wR_2 [$I \geq 2\sigma(I)$][a]	0.0732, 0.1182
V, Å^3	2523.0(9)	R_1, wR_2 (all data)[a]	0.1501, 0.1440
Z	4	$(\Delta/\sigma)_{max}$	0.000

[a] $R_1 = \sum||F_0| - |F_c|| / \sum|F_0|$, $wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$.

Table 2

Selected bond lengths (Å) *and bond angles* (deg.) *for the complex*

Molecule A					
Co1—O1	1.859(3)	O1—Co1—N1	94.6(2)	N1—Co1—N5	178.6(2)
Co1—N1	1.908(3)	O1—Co1—N2	178.6(2)	N1—Co1—N5	88.8(2)
Co1—N2	2.034(4)	O1—Co1—N3	86.7(2)	N2—Co1—N3	92.5(2)
Co1—N3	2.051(4)	O1—Co1—N4	86.2(2)	N4—Co1—N2	92.6(2)
Co1—N4	1.959(3)	O1—Co1—N5	91.5(2)	N4—Co1—N3	85.0(2)
Co1—N5	1.935(4)	N1—Co1—N2	86.6(2)	N5—Co1—N2	89.1(2)
		N1—Co1—N3	93.8(2)	N5—Co1—N3	176.9(2)
				N5—Co1—N4	92.4(2)
Molecule B					
Co2—O2	1.854(3)	O2—Co2—N8	94.4(2)	N8—Co2—N11	178.3(2)
Co2—N8	1.910(4)	O2—Co2—N9	178.8(2)	N8—Co2—N12	90.5(2)
Co2—N9	2.026(4)	O2—Co2—N10	88.1(2)	N9—Co2—N10	92.9(2)
Co2—N10	2.064(4)	O2—Co2—N11	85.5(2)	N11—Co2—N9	93.9(2)
Co2—N11	1.958(3)	O2—Co2—N12	91.3(2)	N11—Co2—N10	84.5(2)
Co2—N12	1.939(4)	N8—Co2—N9	86.2(2)	N12—Co2—N9	87.6(2)
		N8—Co2—N10	93.8(2)	N12—Co2—N10	175.6(2)
				N12—Co2—N11	91.2(2)

pipette. After incubation for 24 h in a thermostat at 25—27 °C, the inhibition (sterile) zone diameters were measured and expressed in mm. An inhibition zone diameter over 7 mm indicates that the tested compound is active against the bacteria under investigation. The antibacterial activities of the compounds were tested against *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, and *Staphylococcus aureus* respectively. The concentration of each solution was 1.0×10^{-3} M.

RESULTS AND DISCUSSION

The Schiff base HL^1 was synthesized by the condensation of equimolar quantities of 2-acetylphenol with N-phenylethane-1,2-diamine in methanol with quantitative yield. We have tried to use the Schiff base and sodium azide to react with cobalt nitrate in various solvents such as methanol, ethanol, chloroform, and acetonitrile, but no single crystals of the final complex were obtained. Accidently, the starting materials 2-acetylphenol with a two-equivalent molar ratio of N-phenylethane-1,2-diamine reacted with cobalt nitrate in methanol in the presence of sodium azide, yielding the red block-shaped single crystals of the cobalt(III) complex with high quality and satisfactory yield. The air and moisture-insensitive complex is crystalline and soluble in a range of common organic solvents such as methanol, ethanol, acetonitrile, DMF, and DMSO, but insoluble in water. In absolute methanol, the complex shows a conductivity value corresponding to the 1:1 electrolytic behavior [10].

IR spectra. The IR spectra of the complex show middle $\nu_{N—H}$ bands at 3127 cm^{-1} and 3163 cm^{-1}, indicating the existence of two different types of amino H atoms. The bands are shifted towards lower frequencies when compared to those observed in the spectra of the HL^1 and L^2 ligands, indicating the coordination of amino nitrogen to the Co atom [11]. An intense band due to $\nu_{C=N}$ at 1613 cm^{-1} is also found to be shifted towards a lower frequency by about 18 cm^{-1} compared to that of the HL^1 ligand, and supports the coordination of azomethine nitrogen of L^1 to the Co atom [12, 13]. A comparison of the IR spectra of HL^1 and the complex reveals the absence of the absorption band associated with the $\nu_{O—H}$ of the phenolic group, indicating the loss of the phenolic proton on complexation due to the formation of the Co—$O_{phenoate}$ bond. This is further supported by a decrease in the $\nu_{C—O}$ frequency by 28 cm^{-1} in the spectra of the complex (1253 cm^{-1}) compared to that of HL^1 (1281 cm^{-1}). The bands at

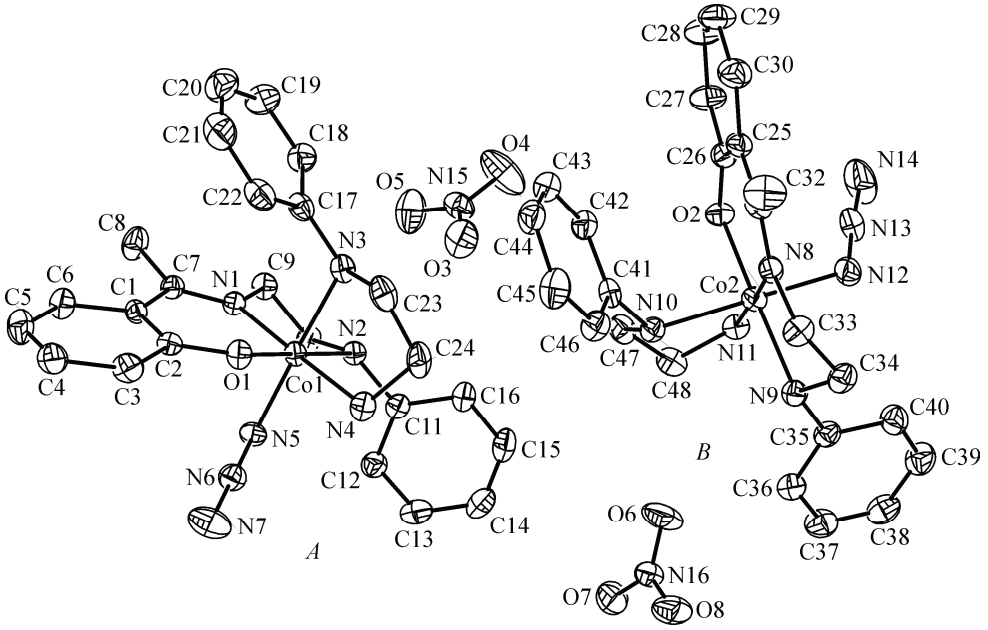

Fig. 1. Molecular structure of the complex with 30 % probability thermal ellipsoids. H atoms are omitted for clarity

454 cm^{-1} and 513 cm^{-1} can be attributed to the $\nu_{Co—O}$ and $\nu_{Co—N}$ respectively. The intense absorption indicative of the azide ligand is at 2023 cm^{-1}.

Structure description of the complex. ORTEP plots with atom numbering of the complex is shown in Fig. 1. The asymmetric unit contains two mononuclear $[CoL^1L^2(N_3)]^+$ cations (molecules A and B) and two nitrate anions. The coordination polyhedron around the Co atom is best described as a distorted octahedron with a CoN_6O chromophore. A distortion from the ideal octahedral geometry is due to the strain created by two five-membered chelate rings Co1—N1—C9—C10—N2 and Co1—N3—C23—C24—N4 in the A molecule, and Co2—N8—C33—C34—N9 and Co2—N10—C47—C48—N11 in the B molecule. The coordination includes one O and two N atoms from L^1, two N atoms from L^2, and one N atom of the azide ligand. The Co atoms are displaced from the mean planes containing the equatorial atoms (N1, N2, N4, and O1 for A; N8, N9, N11, and O2 for B) by 0.016 Å (Co1 in A) and 0.005 Å (Co2 in B). The bond lengths related to the Co atoms are comparable to each other for A and B molecules, and are also comparable to those reported in the cobalt(III) complexes with octahedral coordination [14—16]. The linear (N5=N6=N7 angle of 174.6(5)° and N12=N13=N14 angle of 175.8(6)°) terminal azide ligands are coordinated to the Co atoms in a bent fashion, as evident from the Co—N—N bond angles of 118.0(3)° for A and 117.1(3)° for B.

In the molecular packing structure of the complex, the mononuclear $[CoL^1L^2(N_3)]^+$ cations and the nitrate anions are linked via intermolecular N—H···O hydrogen bonds (Table 3), to form chains running along the *a* axis, as shown in Fig. 2.

Biological activity. The biological activities of HL^1, L^2, and the cobalt(III) complex were tested against the bacteria *Bacillus subtillis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas aereuguinosa*. The results are recorded in Table 4. The data reveal that the cobalt(III) complex has stronger activities than the free ligands. This enhancement of the activity of ligands on complexation can be explained by Overtone′s concept and chelation theory [17]. The theory states that chelation reduces the polarity of the metal atom by the partial sharing of its positive charge with donor groups and possible π-electron delocalization over the whole ring. This results with an increase in the lipophilic character of the complex and favors the penetration of the complex through the lipid layer of the cell membrane. The complex blocks the metal binding sites in the enzymes of microorganisms. Consequently, the complex disturbs the metabolism pathways in the cell and as a result microorganisms die.

T a b l e 3

Hydrogen bond distances (Å) *and angles* (deg.) *for the complex*

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4A···O5[b]	0.90	2.40	3.258(6)	160
N11—H11A···O7[c]	0.90	2.54	3.423(6)	168
N10—H10···O8[d]	0.90(4)	2.04(2)	2.900(5)	160(5)
N9—H9···O7[d]	0.89(3)	2.26(3)	3.037(6)	145(4)
N9—H9···O8[d]	0.89(3)	2.645(18)	3.518(5)	164(4)
N3—H3···O3	0.89(4)	2.03(2)	2.874(5)	158(5)
N2—H2···O3	0.89(3)	2.43(2)	3.295(6)	160(4)
N2—H2···O5	0.89(3)	2.48(3)	3.283(6)	149(4)

Symmetry codes: [b] 1+*x*, *y*, *z*; [c] 1–*x*, 1–*y*, 1–*z*; [d] *x*, 1–*y*, 1–*z*.

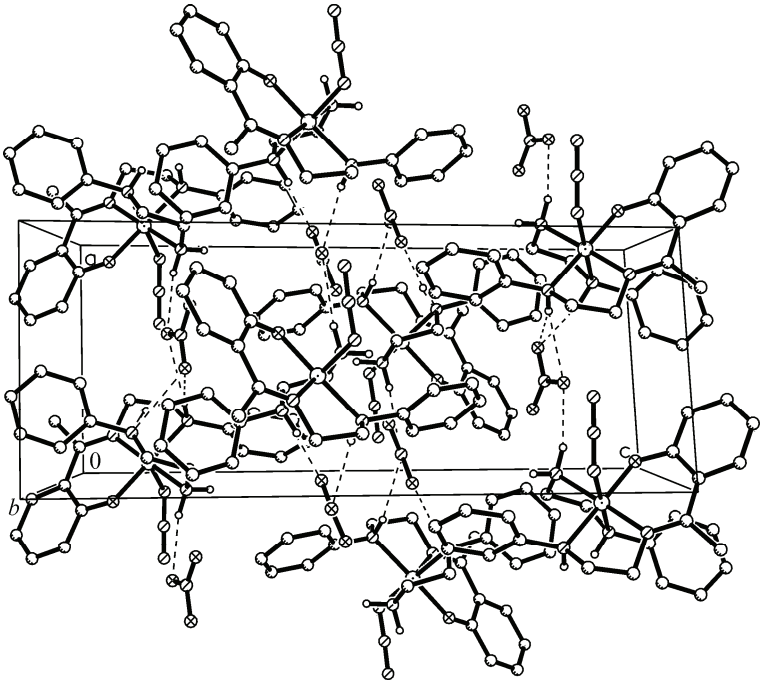

Fig. 2. Molecular packing diagram of the complex, viewed along the *b* axis. Intermolecular hydrogen bonds are drawn as dashed lines

T a b l e 4

Inhibition zone (mm) *of the antibacterial activities*

	Bacillus subtillis	*Staphylococcus aureus*	*Escherichia coli*	*Pseudomonas aereuguinosa*
HL^1	17	13	20	16
L^2	8	5	7	5
$[CoL^1L^2(N_3)]\cdot NO_3$	23	20	26	19

CONCLUSIONS

In the above study, a new azide coordinated cobalt(III) complex with the Schiff base 2-[1-(2-phenylaminoethylimino)ethyl]phenolate and N-phenylethane-1,2-diamine was prepared and structurally characterized. The crystal structure of the complex was determined. The Schiff base coordinates to the Co atom through three N atoms, and N-phenylethane-1,2-diamine coordinates to the Co atom through two N atoms. The antibacterial activities of the ligands and the cobalt(III) complex indicate that the complex shows the enhanced activity in comparison to the free ligands.

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