ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2011, Vol. 37, No. 2, pp. 117–121. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © A.N. Gusev, V.F. Shul'gin, M.A. Kiskin, I.L. Eremenko, 2011, published in Koordinatsionnaya Khimiya, 2011, Vol. 37, No. 2, pp. 119–123.

# Coordination Compound of Cadmium Acetate with the Condensation Product of Salicylaldehyde and 3-(Pyridin-2-yl)-5-(2-aminophenyl)-1H-1,2,4-triazole

**A. N. Gusev**[a], **V. F. Shul'gin**[a, *], **M. A. Kiskin**[b], **and I. L. Eremenko**[b]

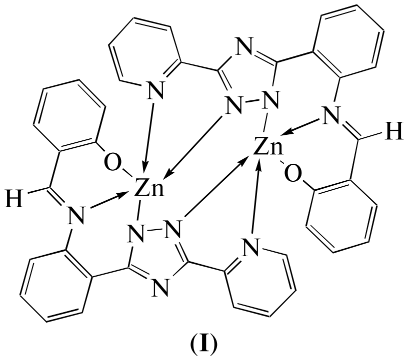
[a] *National Tavrida V. Vernadsky University, ul. Akad. Vernadsky 4, Simferopol, Ukraine*
[b] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia*
* *E-mail: vshul@crimea.edu*

Received June 21, 2010

**Abstract**—The cadmium(II) complex with the condensation product of salicylaldehyde and 3-(pyridine-2-yl)-5-(2-aminophenyl)-1H-1,2,4-triazole ($H_2L$), $Cd_2(H_2L)_2(OAc)_4 \cdot 3EtOH$, is synthesized. Its crystal structure is studied by X-ray diffraction analysis. In the centrosymmetric binuclear complex (Cd···Cd 3.938(1) Å), the Cd atoms are bonded by two tridentate bridging acetate anions. Two other acetate anions are terminal and coordinated by the monodentate mode. The coordination polyhedron of the Cd atom is a distorted octahedron. The triazole ligands are bonded to the cadmium cations through the N atoms of the pyridine cycle and triazole ring.

**DOI:** 10.1134/S1070328411010052

Polyfunctional derivatives of 1,2,4-triazole form a new class of organic ligands. A variety of coordination modes makes it possible to obtain related complexes interesting from the theoretical and practical point of views due to their unique magnetic, optical, and biological properties [1–5]. The zinc complex with 3-(pyridine-2-yl)-5-(2-salicylideneiminophenyl)-1H-1,2,4-triazole (**I**), which is the condensation product of salicylaldehyde and 3-(pyridine-2-yl)-5-(2-aminophenyl)-1H-1,2,4-triazole (**$H_2$L**), has recently been described. This compound exhibits high photo- and electroluminescence activities [5]. According to the X-ray diffraction data, complex **I** has a binuclear structure, and the zinc cations are coordinated by two bridging ligands existing in the doubly coordinated form [6].



**(I)**

In this work we present the results of studying the coordination compound of cadmium acetate with the molecular form of the condensation product of salicylaldehyde and 3-(pyridine-2-yl)-5-(2-aminophenyl)-1H-1,2,4-triazole, $Cd_2(H_2L)_2(OAc)_4 \cdot 3EtOH$ (**II**).

## EXPERIMENTAL

Complex **II** was synthesized in air in purified 96% ethanol. Salicylaldehyde and $Cd(OAc)_2 \cdot 2H_2O$ (reagent grade) were used. 3-(Pyridin-2-yl)-5-(2-aminophenyl)-1H-1,2,4-triazole was synthesized according to a procedure described earlier [7].

IR spectra were recorded in the range from 4000 to 400 cm$^{-1}$ on a Nicolet Nexus 470 FTIR spectrophotometer using a standard molding procedure of the sample with KBr.

NMR spectra were detected on a Bruker VXR-400 spectrometer (400 MHz) using $Me_4Si$ as an internal standard and DMSO-$d_6$ as a solvent.

The cadmium content was calculated from the data of trilonometric titration after the thermal decomposition of a weighed sample. The nitrogen content was determined by the Dumas micromethod.

**Synthesis of $H_2$L.** Salicylaldehyde (0.512 g, 4.2 mmol) was added with stirring to a solution of 3-(pyridine-2-yl)-5-(2-aminophenyl)-1H-1,2,4-triazole (0.948 g, 4 mmol) in EtOH (20 ml) heated to 60–70°C. The reaction mixture was stirred on heating with a reflux condenser for 1 h. The solution was cooled, and the precipitate that formed was filtered off, washed with cool ethanol, and dried in air. Colorless crystals with mp = 237°C were obtained. The yield was 1.18 g (87%).

**Table 1.** Selected crystallographic data and experimental characteristics for complex **II**

| Parameter | Value |
|---|---|
| Molecular weight | 1281.92 |
| Temperature, K | 150(2) |
| Crystal size, mm | 0.40 × 0.20 × 0.20 |
| Crystal system | Monoclinic |
| Space group | *C*2/*c* |
| *a*, Å | 26.1536(10) |
| *b*, Å | 21.4975(8) |
| *c*, Å | 10.0212(4) |
| β, deg | 97.3050(10) |
| *V*, $Å^3$ | 5588.6(4) |
| Z | 4 |
| $\rho_{calcd}$, $g/cm^3$ | 1.524 |
| μ, $cm^{-1}$ | 8.33 |
| *F*(000) | 2616 |
| θ, deg | 1.23–30.61 |
| Ranges of indices | $37 \le h \le 33, -30 \le k \le 30,$<br>$-14 \le l \le 11$ |
| Total number of reflections | 22493 |
| Number of independent reflections | 8343 ($R_{int} = 0.0208$) |
| Number of reflections with $I \ge 2\sigma(I)$ | 6942 |
| $T_{min}/T_{max}$ | 0.7317/0.8511 |
| Number of refined parameters | 370 |
| Goodness-of-fit | 1.026 |
| $R$ ($I \ge 2\sigma(I)$) | $R_1 = 0.0376, wR_2 = 0.1283$ |
| $R$ (all data) | $R_1 = 0.0471. wR_2 = 0.1441$ |
| $\Delta\rho_{min}/\Delta\rho_{max}$, $e\,Å^{-3}$ | −1.203/1.813 |

$^1$H NMR, δ, ppm: 10.1 s (br, OH), 8.65 d ($1H_{arom}$), 8.12 d ($1H_{arom}$), 7.90 dt ($1H_{arom}$), 7.80 d ($1H_{arom}$), 7.40 m ($2H_{arom}$), 7.20 m ($2H_{arom}$ + ($C^2$–H)), 6.95 m ($2H_{atom}$ + (N–H)), 6.85 t ($1H_{arom}$), 6.80 t ($1H_{arom}$). IR, ν, $cm^{-1}$: 3380 ν(OH), 3270 ν(NH), 3056 ν(C–H), 1629 ν(C–N), 1292 ν(C–O).

**Synthesis of di-μ-acetato-diacetato-bis[5-(2'-hydroxyphenyl)-2-(2'-pyridyl)-7,8-benzo-6,5-dihydro-1,3,6-triazaindolizine]dicadmium (solvate with ethanol), $Cd_2(H_2L)_2(OAc)_4 \cdot 3EtOH$ (II).** $Cd(OAc)_2 \cdot 2H_2O$ (0.8 g, 3 mmol) was added to a suspension of $H_2L$ (1.05 g, 3 mmol) in EtOH (10 ml), and the mixture was stirred on heating for 2 h. A precipitate that formed was left to stay overnight under the mother liquor, then filtered off, washed with ethanol, and dried in air. The yield of the complex was 1.4 g (75%). Recrystallization from 96% ethanol gave light yellow crystals of prismatic habitus suitable for X-ray diffraction analysis.

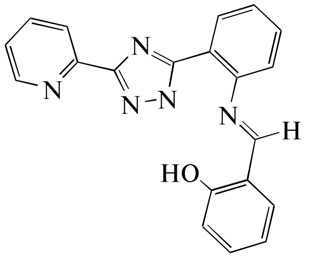
| For $C_{54}H_{60}Cd_2N_{10}O_{13}$ | | |
|---|---|---|
| anal. calcd. (%): | Cd, 17.54; | N, 10.92. |
| Found (%): | Cd, 17.22; | N, 11.18. |

IR, ν, $cm^{-1}$ : 3300 ν(NH), 3060 ν($C–H_{arom}$), 1630 ν(C–N), 1548 $\nu_{as}(COO^-)$, 1420 $\nu_s(COO^-)$, 1284 ν($C_{arom}$–O).

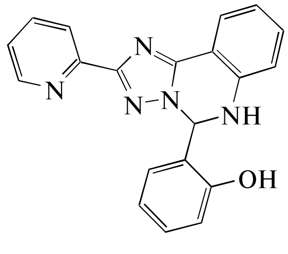
**X-ray diffraction analysis.** An experimental array of reflection was obtained by the standard method [8–10] on a Bruker SMART APEX II automated diffractometer equipped with a CCD detector and a monochromatic radiation source (Mo$K_\alpha$ radiation, λ = 0.71073 Å). The structure of complex **II** was solved by a direct method and refined in the full-matrix anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms of the carbon-containing ligands were geometrically generated and refined in the riding model. The calculations were performed using the SHELX-97 program package. The crystallographic parameters and X-ray diffraction experimental parameters are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. The complete set of X-ray diffraction data was deposited with the Cambridge Crystallographic Data Centre (no. 783744; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

The study of the condensation product of salicylaldehyde with 3-(pyridine-2-yl)-5-(2-aminophenyl)-1H-1,2,4-trLiazole and the related complexes showed that the compound can exist in two isomeric forms: linear azomethine **(A)** and cyclic dihydrotriazaindolizine **(B)**



**(A)**



**(B)**

According to the data of $^1$H NMR spectroscopy, in solutions compound $H_2L$ exists in the cyclic form. The spectrum contains no signal of the hydrogen atom of the triazole cycle, which usually appears at 13–14 ppm, but the signal of the H atom of the secondary

**Table 2.** Selected bond lengths and bond angles for complex **II***

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| Cd(1)–O(4) | 2.2497(19) | N(3)–N(4) | 1.352(2) |
| Cd(1)–O(1) | 2.279(2) | N(4)–C(11) | 1.349(3) |
| Cd(1)–N(1) | 2.307(2) | N(4)–C(22) | 1.470(3) |
| Cd(1)–O(2)$^{\#1}$ | 2.328(2) | N(5)–C(21) | 1.367(3) |
| Cd(1)–N(2) | 2.3717(18) | N(5)–C(22) | 1.459(3) |
| Cd(1)–O(2) | 2.587(2) | O(1)–C(1) | 1.257(3) |
| N(1)–C(5) | 1.338(3) | O(2)–C(1) | 1.264(3) |
| N(1)–C(9) | 1.349(3) | O(3)–C(3) | 1.242(4) |
| N(2)–C(11) | 1.340(3) | O(4)–C(3) | 1.283(3) |
| N(2)–C(10) | 1.367(3) | O(5)–C(28) | 1.354(3) |
| N(3)–C(10) | 1.322(3) | | |
| Angle | ω, deg | Angle | ω, deg |
| O(4)Cd(1)O(1) | 86.59(7) | C(5)N(1)Cd(1) | 123.28(17) |
| O(4)Cd(1)N(1) | 125.63(7) | C(9)N(1)Cd(1) | 117.70(15) |
| O(1)Cd(1)N(1) | 147.17(7) | C(11)N(2)C(10) | 103.14(19) |
| O(4)Cd(1)O(2)$^{\#1}$ | 103.82(7) | C(11)N(2)Cd(1) | 144.93(15) |
| O(1)Cd(1)O(2)$^{\#1}$ | 92.80(7) | C(10)N(2)Cd(1) | 111.62(14) |
| N(1)Cd(1)O(2)$^{\#1}$ | 85.81(7) | C(10)N(3)N(4) | 101.85(18) |
| O(4)Cd(1)N(2) | 99.15(7) | C(11)N(4)N(3) | 111.59(18) |
| O(1)Cd(1)N(2) | 98.32(7) | C(11)N(4)C(18) | 127.71(19) |
| N(1)Cd(1)N(2) | 72.73(7) | N(3)N(4)C(18) | 120.68(18) |
| O(2)$^{\#1}$Cd(1)N(2) | 155.00(7) | C(17)N(5)C(18) | 126.1(2) |
| O(4)Cd(1)O(2) | 138.77(7) | O(1)C(1)O(2) | 122.0(3) |
| O(1)Cd(1)O(2) | 53.43(7) | O(1)C(1)C(2) | 118.2(3) |
| N(1)Cd(1)O(2) | 95.41(7) | O(2)C(1)C(2) | 119.8(3) |
| O(2)$^{\#1}$Cd(1)O(2) | 72.35(8) | O(3)C(3)O(4) | 121.8(2) |
| N(2)Cd(1)O(2) | 96.57(7) | O(3)C(3)C(4) | 121.1(3) |
| Cd(1)O(2)$^{\#1}$Cd(1)$^{\#1}$ | 106.37(8) | O(4)C(3)C(4) | 117.1(3) |
| C(5)N(1)C(9) | 118.8(2) | | |

* Symmetry transformations of equivalent atoms: $^{\#1}$ $-x, y, -z + 3/2$.

amine is observed at 6.95 ppm. In addition, the singlet signal of the C(2)–H proton of dihydrotriazaindolizine is observed at 7.2 ppm. This region is characteristic of the related heterocyclic systems [11].

The dihydrotriazaindolizine form of the ligand was found for the crystal structure of its complex with cadmium(II) acetate. According to the X-ray diffraction data, the complex is binuclear and crystallizes as a solvate with three ethanol molecules. The molecule of the complex is centrosymmetric. The cadmium atoms (Cd···Cd 3.938(1) Å) are bonded by two tridentate bridging acetate anions (Cd(1)–O(1) 2.279(2), Cd(1)–O(2)$^{\#1}$ 2.329(2), Cd(1)–O(2) 2.587(2) Å) (Fig. 1, Table 2) coordinated by the $3_2$-*c* type [12]. Two more acetate anions are coordinated according to the monodentate type (Cd(1)–O(4) 2.2497(19) Å).

The heterocyclic ligand H$_2$L is coordinated by the bidentate mode and bound to the cadmium cation through the N(1) atom of the pyridine cycle and the N(2) atom of the triazole cycle, which is not characteristic of nonfunctional triazoles. The Cd(1)–N(2) bond (2.3717(18) Å) is substantially longer than Cd(1)–N(1) (2.307(2) Å).

The cadmium ion coordinates four oxygen atoms of the acetate anions and two nitrogen atoms of triazole arranged at the vertices of the strongly distorted

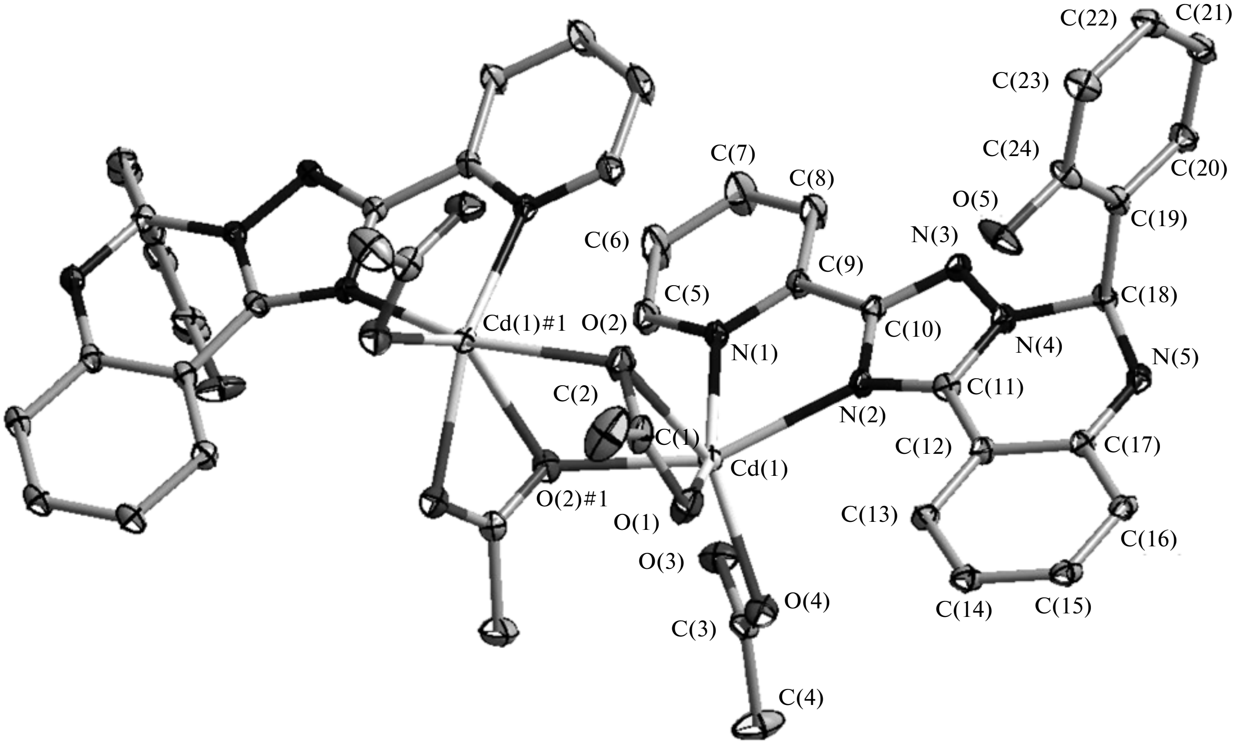


**Fig. 1.** Molecular structure of complex **II** (hydrogen atoms are omitted, thermal ellipsoids at 30% probability).

octahedron. The four-membered $Cd_2O_2$ cycle is asymmetric and noticeably bent. The dihedral angle between the O(2)–Cd(1)–O(2)$^{\#1}$ and O(2)–Cd(1)$^{\#1}$–O(2)$^{\#1}$ planes is 14.8°, and the OCdO bond angle is 72.35(8)°. The triazole, phenyl, and pyridyl cycles lie almost in the same plane, and the 2-hydroxyphenyl fragment is turned relative to the pyridyl ring by 89.1° (Fig. 1). The N(3)–N(4) bond (1.352(3) Å) is noticeably shorter than the standard nitrogen–nitrogen ordinary bond (1.451 Å) [13], which can be due to double bond delocalization in the triazole fragment. The C(18)–N(4) bond (1.470(3) Å) is appreciably elongated compared to the standard value. The other bonds in the organic ligands have standard values.

One of the outer-sphere ethanol molecules is disordered. The crystalline lattice is stabilized by the system of intermolecular hydrogen bonds (Table 3) and nonvalent interactions between the conjugated nitrogen-containing heterocycles of the adjacent molecules of the complex, whose planes are almost parallel and lie at a distance of ~3.5 Å (π-stacking interactions) (Fig. 2).

Thus, the studies performed show that the reaction of 3-(pyridine-2-yl)-5-(2-aminophenyl)-1H-1,2,4-triazole with salicylaldehyde affords dihydro-1,3,6-triazaindolizine heterocyclic system, which is retained upon coordination by the cadmium cation. The reaction with zinc acetate results in the decomposition of the heterocycle and coordination of functionalized

**Table 3.** Hydrogen bond geometry in structure **II**

| Contact D–H···A | Distance, Å | | | Angle DHA, deg | Coordinates of atom A |
|---|---|---|---|---|---|
| | D–H | H···A | D···A | | |
| N(5)–H(5)···O(4) | 0.88 | 2.14 | 3.013(3) | 172 | $-x + 1/2, -y + 1/2, -z + 2$ |
| O(5) –H(5*B*)···O(3) | 0.84 | 1.81 | 2.645(3) | 179 | $x, y, z + 1$ |
| O(5)···O(2S)* | | | 2.061(5) | | $x, y, z$ |
| O(4)···O(1S)* | | | 2.893(5) | | $x, y, z$ |

* Hydrogen atoms of ethanol molecules were not found.

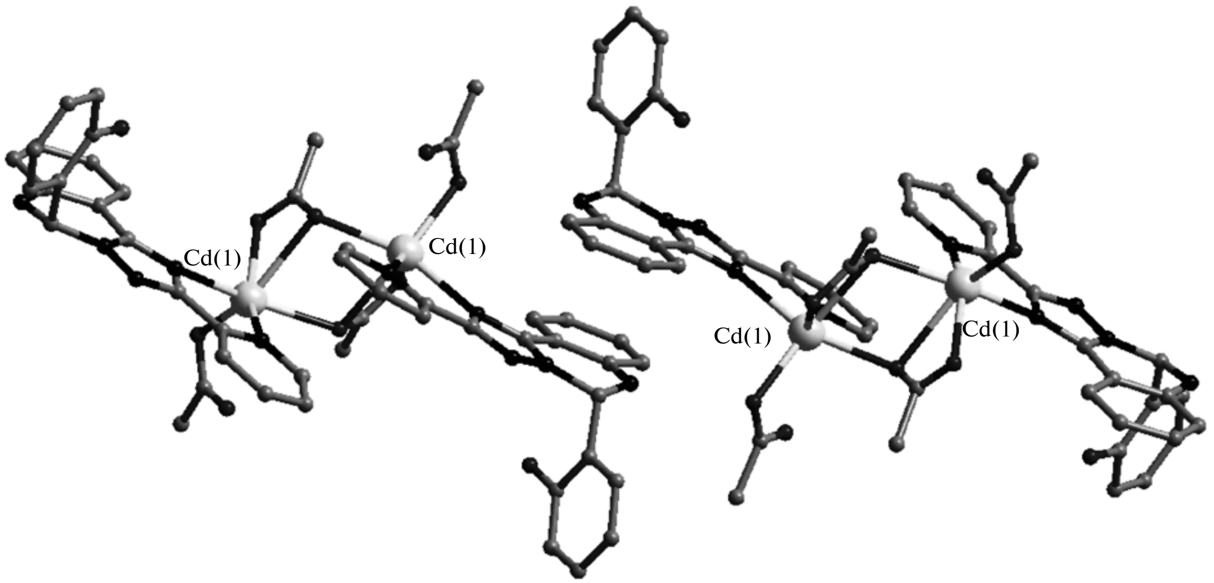


**Fig. 2.** Fragment of the molecular packing of crystalline complex **II**.

triazole in the doubly deprotonated azomethine form (complex **I**).

## REFERENCES

1. Kahn, O., Krober, J., and Jay, C., *Adv. Mater.*, 1992, vol. 4, p. 718.
2. Haasnoot, J.G., *Coord. Chem. Rev.*, 2000, vols. 200–202, p. 131.
3. Han, H., Song, Y., Hou, H., et al., *Dalton Trans.*, 2006, p. 1972.
4. Yi, L., Zhu, L.N., Ding, B., et al., *Inorg. Chem. Commun.*, 2003, vol. 6, p. 1209.
5. Gadirov, R.V., Degtyarenko, R.V., Eremina, N.S., et al., *Atomic and Molecular Pulsed Lasers (Russia)*, 2009, p. 47.
6. Gusev, A.N., Eremenko, I.L., Kiskin, M.A., et al., *Uchenye Zapiski Tavricheskogo Nats. Un-Ta Im. V.I. Vernadskogo, Ser. Biologiya I Khimiya*, 2009. vol. 22, no. 61, p. 154.
7. Baldwin, J., Pat. 4.198.513 USA. Assignee: Merck & Co., Inc. Rahway (NJ, USA), 1980.
8. *SMART (control) and SAINT (integration) Sofware. Version 5.0*, Madison (WI, USA): Bruker AXS Inc., 1997.
9. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, vol. 46, p. 467.
10. Sheldrick, G.M., *SHELXL-97. Program for the Refinement of Crystal Structures*, Göttingen (Gormany): Univ. of Göttingen, 1997.
11. Smirnov, G.A., Sizova, E.P., Luk'yanov, O.V., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2003, p. 2311.
12. Porai-Koshits, M.A., *Zh. Strukt. Khim.*, 1980, vol. 21, p. 146.
13. Orpen, G., Brammer, L., Allen, F.H., et al., *J. Chem. Soc., Dalton Trans.,* 1989, p. S1.