

Research Article

L-Valine and Salicylaldehyde Derivative Schiff Base Zn(II) Complexes as UVA Sunscreen

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Abstract

Ultraviolet (UV) of sunlight is classified into UVC, UVB and UVA according to wavelength. Sunscreen cosmetics must protect our skin against damage such as stains and freckles caused by UVB light or wrinkles caused by UVA light. Commonly sunscreen cosmetics are composed of inorganic UV-reflecting compounds and organic UV-absorbing ones. Although many good materials of both types of compounds for UVB protection are known, only a few UVA-absorbing organic compounds are known in spite of serious hazard of UVA light. We have prepared six Zn(II) complexes having tridentate Schiff base ligands from L-valine and (H-, Cl- and CH₃O-) salicylaldehyde derivatives and monodentate ligands (methanol or imidazole). These pale yellow compounds have broad absorption (charge transfer) band around 300-400 nm, which covers UVA wavelength region (315-400 nm) fully. In contrast to the analogous Cu(II) complexes acting as photocatalysts, small degree of photo-induced reactions of only Zn(II) complexes (leaving imidazole to replace methanol) as well as composite of Zn(II) complexes and TiO₂ could be observed after UV light (< 350 nm) irradiation up to 60 min. By mixing with anatase TiO₂ powder, as scattering (or absorption) compounds for protecting from UVB light, which act as relatively stable UVA sunscreen. To our knowledge about UVA sunscreen, a Zn(II) complex covering UVA wavelength region completely is developed for the first time.

Keywords: Zinc(II); L-Valine; TiO₂; UVA; Sunscreen

Abbreviations:

UV: Ultraviolet

Introduction

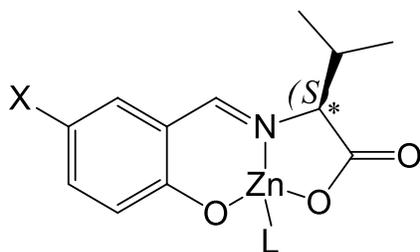
Generally UV of sunlight is classified into UVC, UVB and UVA according to wavelength. Especially, UVB (280 nm-315 nm) and UVA (315 nm-400 nm) are attracting much attention because of influence on human health and environmental issues. Sunscreen cosmetics are required useful functions to protect our skin against damage such as stains and freckles by UVB light or wrinkles by UVA light.

Commonly sunscreen cosmetics are composed of inorganic UV-reflecting compounds and organic UV-absorbing ones.

Conventionally, commercially available UV intercepting ones out of the skin are known as UV-reflecting ones, for instance, TiO₂, ZnO and so on. While as for organic UV-absorbing ones, ethylhexylmethoxycinnamate, octylmethoxycinnamate, tert-butylmethoxydibenzoylmethane, and so on are known. UVA denatures protein and lets skin age by arriving at the dermis layer of skin. In spite of serious hazard of UVA light, only a few food ones are known as organic UVA-absorbing ones, though many good ones are known as UVB-absorbing (or reflecting) ones. Thus UVA-absorbing ones that can cover *all range of UVA wavelength region* are needed so far [1].

In this way, we focused on metal complexes, having both aspects of organic and inorganic compounds, as UVA-absorbing ones. Indeed, recently we have found that composite materials of *L*-amino acid derivative Schiff base Cu(II) complexes and TiO₂ occur characteristic photo-induced electron transfer reactions by absorbing UV(A) light [2]. Unfortunately, these Cu(II) complexes were greenish blue, which is not suitable for whitening cosmetics. Colourless Zn(II) ions or complexes may be suitable for this purpose.

Herein, we report on the analogous *L*-valine amino acid derivative Schiff base Zn(II) complexes (X = H-, Cl-, and CH₃O-; L = methanol, imidazole) which are expected both biocompatibility (from amino acid moiety) and whitening effect (Scheme 1). We have discussed the substituent (X-, L-) effects on absorption and emission wavelength and intensity, and investigated photo-induced reaction as composites and anatase TiO₂.



Scheme 1. Molecular structures of Zn(II) complexes (X= H-, Cl-, or CH₃O-; L= methanol or imidazole).

Materials and Methods

Preparation of three Zn(II) complexes (L=methanol) was carried out by following conventional procedures [3]. To a methanol solutions (50 mL) of *L*-valine (3 mmol) and salicylaldehyde (X=H) (or 5-chloro-salicylaldehyde (X=Cl), 5-methoxy-salicylaldehyde (X=CH₃O) (3 mmol) stirred for 3 hr at 333 K, zinc(II) acetate monohydrate (3 mmol) was added and stirred for 3 hr to give rise to yellow crude products. After evaporation for concentration and recrystallization from methanol, yellow products were obtained. On the other hand, the corresponding three Zn(II) complexes (L=imidazole) were prepared in a similar procedure except for addition of imidazole (3 mmol) at 1 hr after addition of zinc(II) acetate monohydrate for easy isolation. Formation of complexes was confirmed by C=N bands of IR spectra around 1630 cm⁻¹. Due to quite easy dissociation and/or di- or tri-merization of the monodentate "L" ligands in solution, ¹H-NMR (not shown) could not be observed properly like normal and stable compounds. Hence we managed to measure IR spectra in the solid state as follows (cm⁻¹): X=H; L=imidazole: 1630 (C=N), 3414 (O-H). X=H; L=methanol: 1633 (C=N), 3306 (O-H). X=Cl; L=imidazole: 1629 (C=N), 3422 (O-H). X=Cl; L=methanol: 1635 (C=N), 3441 (O-H). X=CH₃O; L=imidazole: 1632 (C=N), 3422 (O-H). X=CH₃O; L=methanol: 1634 (C=N), 3434 (O-H).

Infrared spectra were recorded on a JASCO FT-IR 2400 spectrophotometer in the range of 4000-400cm⁻¹ at 298K as KBr pellets. Absorption electronic spectra were measured on a JASCO V-570 spectrophotometer in the range of 900-250 nm at 298K. Fluorescent spectra were measured on a JASCO FP-6200 spectrophotometer in the range of 350-600 nm at 298K. ¹H-NMR was measured on a JEOL JMN-300 spectrometer (300 MHz) in DMSO-d₆. UV light source used was Hayashi LA-310UV with a visible light (> 350 nm) cut filter.

Prismatic pale yellow single crystal of X=H; "L=H₂O" (as isolated crystals which were grown from X=H; L=methanol in methanol (containing water) solution) were glued on top of a glass fiber and coated with a thin layer of epoxy resin to measure the diffraction data. Intensity data were collected on a Bruker APEX2 CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data analysis was carried out with a SAINT program package. The structures were solved by direct methods with a SHELXS-97 [5] and expanded by Fourier techniques and refined by full-matrix least-squares methods based on F² using the program SHELXL-97 [5]. An empirical absorption correction was applied by a program SADABS [6]. All non-hydrogen atoms were readily located and refined by anisotropic thermal parameters. All hydrogen atoms were located at geometrically calculated positions and refined using riding models.

Crystallographic data for X=H; L=H₂O. C₁₂H₁₅NO₄Zn. crystal size 0.30 mm \times 0.17 mm \times 0.11 mm, Mw = 834.75, trigonal, space group P3₁ (#144), a = 12.655(3) \AA , c = 6.7673(15) \AA , V = 938.6(5) \AA^3 , Z = 3, Dcalc = 1.606 mg/m³, F(000) = 468, R1 = 0.0259, wR2 = 0.0707 (2628 reflections), S = 1.490, Flack parameter = 0.026(7). (where R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. Rw = $(\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, w = 1/($\sigma^2(F_o) + (0.1P)^2 + 0.4679P$), P = (F_o² + 2F_c²)/3).

Results and Discussion: As shown structure of a bridged five-coordinated complex in Figure 1, Schiff base Zn(II) complexes (X = H-, Cl-, and CH₃O-; L = imidazole) were pale yellow showing red-shift of electronic spectra by electron donating group (Figure 2), and the corresponding CD spectra appeared negative Cotton effect around 280 and 380 nm. They also appeared blue emission around 380 nm and 470 nm by UV light excitation, of which intensity was strong for X= CH₃O. It should be noted that absorption electronic spectra appeared broad (charge transfer) bands around 300-400 nm, which covers UVA wavelength region (315-400 nm) except for intense (Π - Π^* or n- Π^*) bands of UVB or UVC region. Contrary to known UVA-absorbing Zn(II) complexes reported in patents showing more intense Π - Π^* or n- Π^* bands but limited up to shorter wavelength (less than 400 nm), the present Zn(II) complexes are possible to cover fully wide range of UVA wavelength region. To our knowledge, this is the first example of such UVA-absorbing Zn(II) complexes.

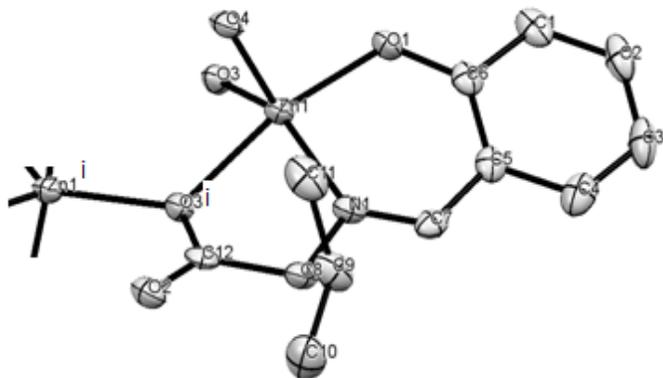


Figure 1. Crystal structure of "X=H; L=H₂O" one showing selected atom labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond distance (Å) and bond angles (°): Zn1-O1 = 1.998(3), Zn1-O4 = 2.013(3), Zn1-N1 = 2.021(3), Zn1-O3ⁱ = 2.035(2), Zn1-O3 = 2.151(3), O1-Zn1-O4 = 103.68(11), O1-Zn1-N1 = 91.82(12), O4-Zn1-N1 = 108.38(12), O1-Zn1-O3ⁱ = 91.80(11), O4-Zn1-O3ⁱ = 104.88(12), N1-Zn1-O3ⁱ = 144.61(12), O1-Zn1-O3 = 168.32(10), O4-Zn1-O3 = 84.75(10), N1-Zn1-O3 = 77.70(11), O3-Zn1-O3ⁱ = 93.83(11). Symmetry operation: (i) 1-y, x-y+1, z+1/3.

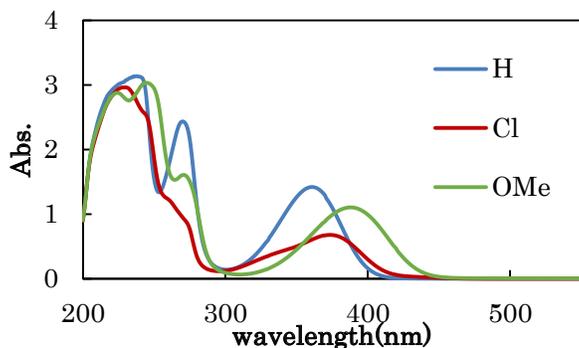


Figure 2. Absorption electronic spectra (0.2 M methanol solutions) for Zn(II) complexes (X= H-, Cl-, or CH₃O-; L= methanol).

Consequently, composite materials of anatase TiO₂ powder and these Zn(II) complexes can be also expected for potential application of sunscreen for wide range UVA-UVB-UBC. However, the spectra of composite materials (0.2 mM Zn(II) complexes and 0.05 mM TiO₂ in methanol suspension) were changes with decreasing π - π^* and charge transfer bands and increasing intensity between them around 300 nm after UV light irradiation up to 60 nm (Figure 3).

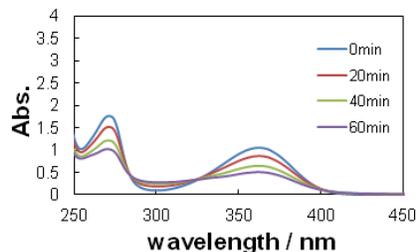


Figure 3. Spectra changes of methanol suspension of TiO₂ and Zn(II) complex (X= H-; L= imidazole) after UV light irradiation for 0, 20, 40, and 60 min.

Although spectral changes occurred, and serious change was observed for X= CH₃O especially, they are attributed not to photo-induced electron transfer reactions (accompanying with reduction from Cu(II) to Cu(I)) like the analogous Cu(II) complexes [2] but to decomposition of monodentate ligand (L) of Zn(II) complex by exchanging imidazole ligand and methanol solvent only. It may be caused by unstability of imidazole ligands.

Therefore, we employed Zn(II) complexes (L=methanol) from the beginning. Figure 4 depicts absorption electronic spectra in methanol solutions. Similar to the complexes (L=imidazole), these also appeared characteristic band around UVA wavelength regions and substitution group effects on both absorption and emission spectra, though relatively smaller spectral changes could be observed after UV light irradiation up to 60 min as suspension with TiO₂.

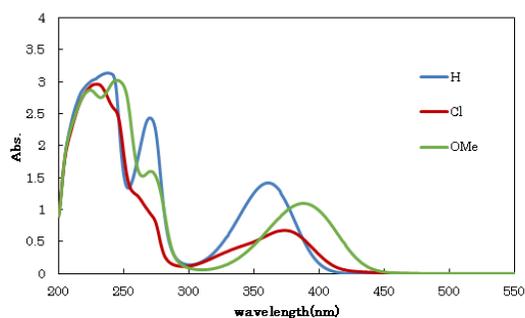


Figure 4. Absorption electronic spectra (0.2 M methanol solutions) for Zn(II) complexes (L= methanol).

Conclusion

Consequently, all of the present Zn(II) complexes showed relatively strong absorption fully over the wavelength range of UVA region (315nm-400nm). In addition, monodentate ligands (X=methanol) has advantage of hard to photo-decomposition (or changes) without losing function of UVA absorption. Since these complexes did not exhibit photo-induced electron transfer reactions under coexisting TiO₂, they were suggested to utility to new sunscreen cosmetics especially against UVA light [4].

Acknowledgements

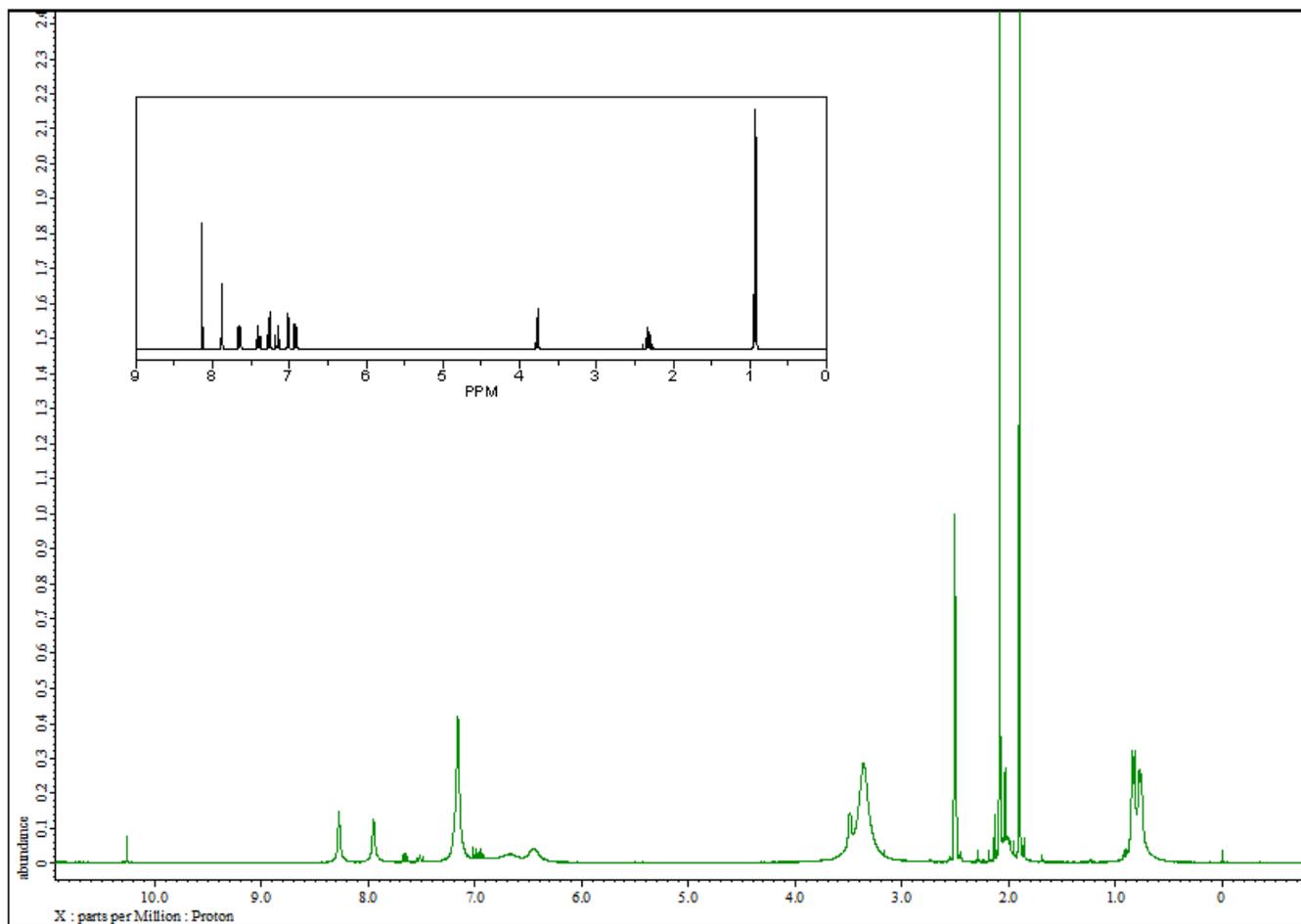
This work was partly supported by Network Joint Research Center for Materials and Devices (Tokyo Institute of Technology).

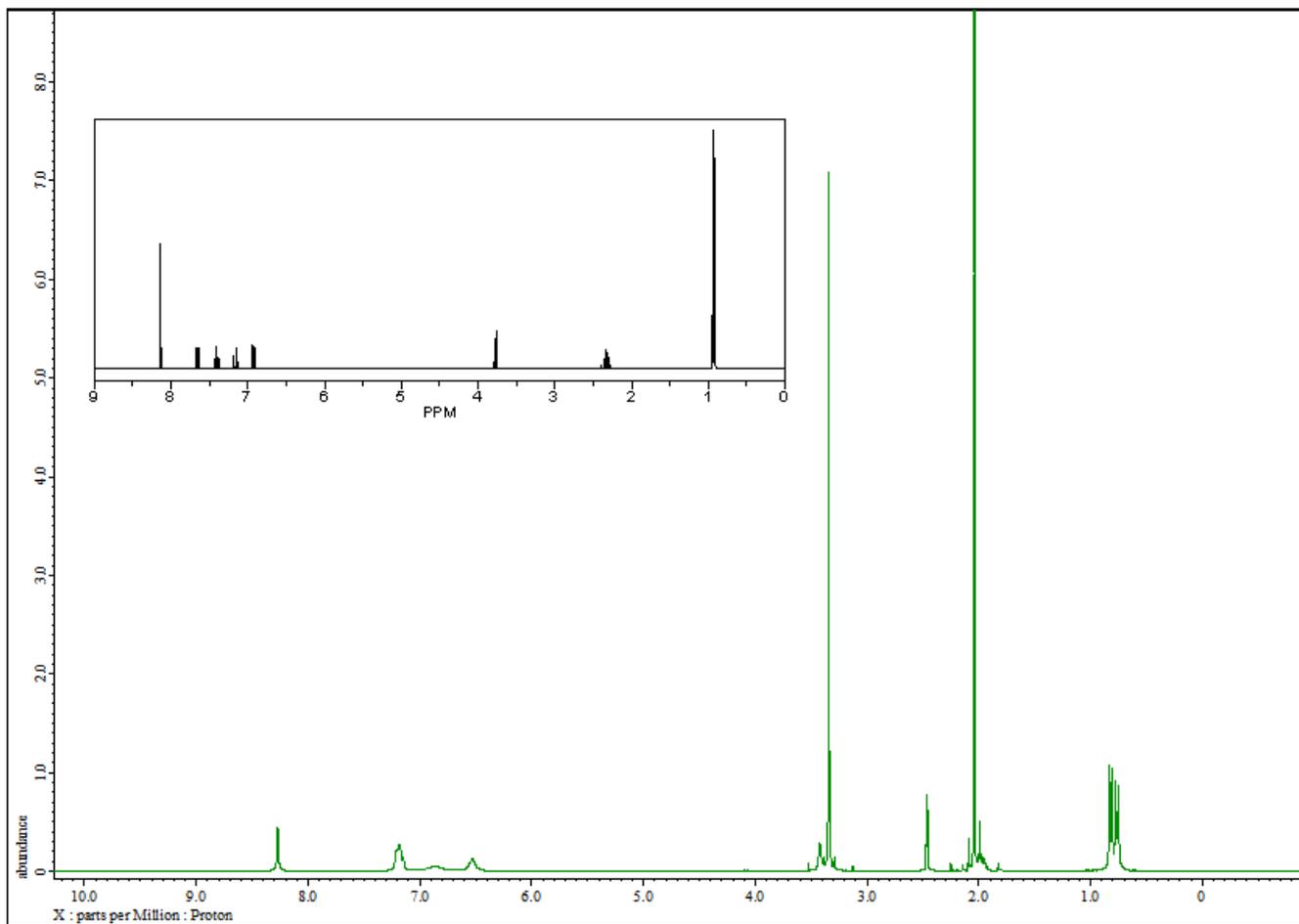
Conflict of Interest

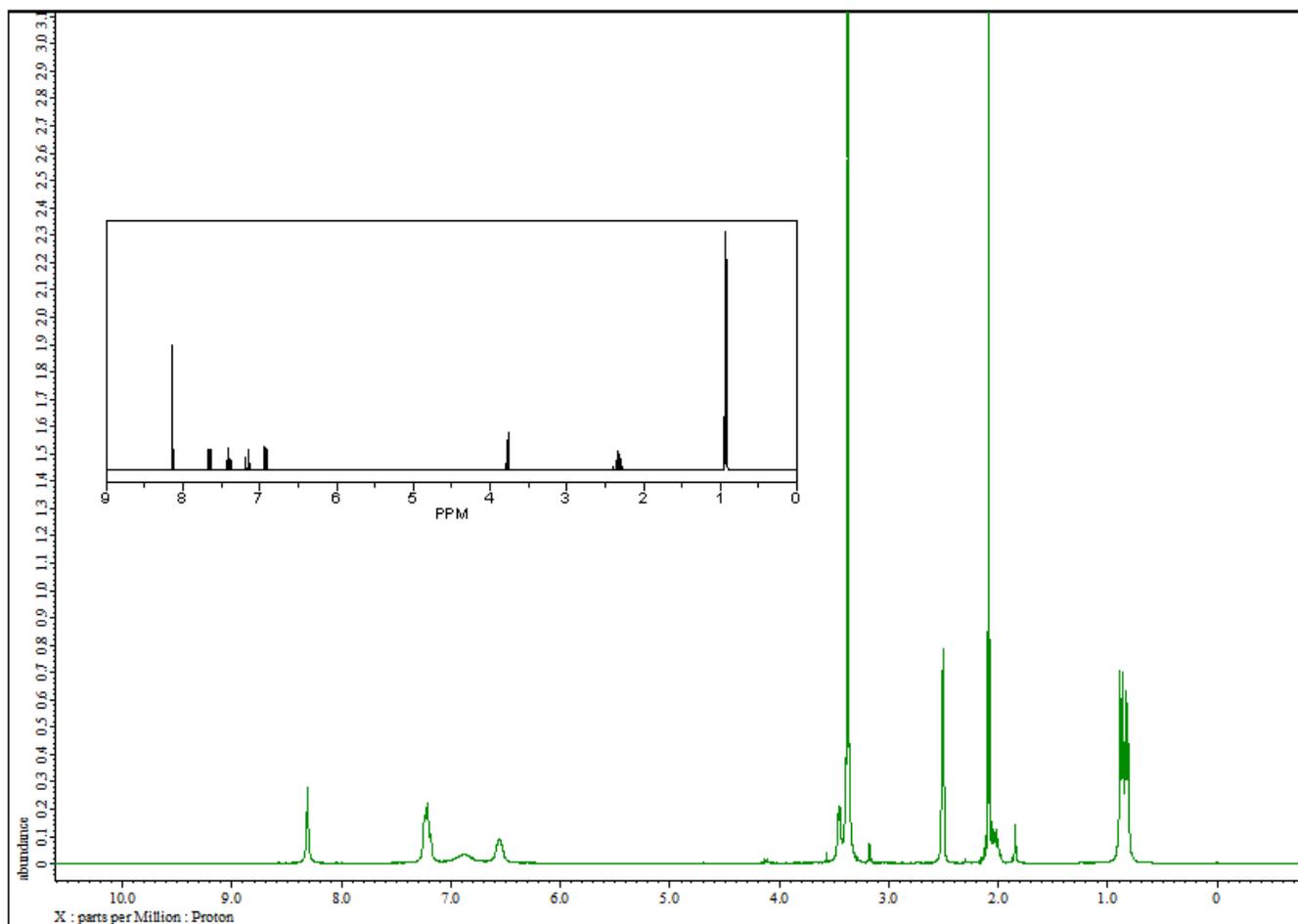
None.

Supplementary data

CCDC 1510939 contains the supplementary crystallographic data. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.







References

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checkCIF

Structure factors have been supplied for datablock(s) I

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: C-C = 0.0067 Å Wavelength=0.71073

Cell: a=12.655 (3) b=12.655 (3) c=6.7673 (15)
 alpha=90 beta=90 gamma=120

Temperature: 100 K

	Calculated	Reported
Volume	938.6 (6)	938.6 (5)
Space group	P 31	P 31
Hall group	P 31	P 31
Moiety formula	C12 H15 N O4 Zn	C12 H15 N O4 Zn
Sum formula	C12 H15 N O4 Zn	C12 H15 N O4 Zn
Mr	302.64	302.62
Dx, g cm ⁻³	1.606	1.606
Z	3	3
Mu (mm ⁻¹)	1.968	1.968
F000	468.0	468.0
F000'	469.04	
h, k, lmax	16, 16, 8	16, 16, 8
Nref	2884 [1442]	2738
Tmin, Tmax	0.676, 0.805	0.680, 0.808
Tmin'	0.549	

Correction method= # Reported T Limits: Tmin=0.680 Tmax=0.808
AbsCorr = EMPIRICAL

Data completeness= 1.90/0.95 Theta (max)= 27.560

R(reflections)= 0.0259 (2628) wR2(reflections)= 0.0726 (2738)

S = 0.552 Npar= 170

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

GOODF01_ALERT_2_B The least squares goodness of fit parameter lies
 outside the range 0.60 <> 4.00
 Goodness of fit given = 0.552
 PLAT987_ALERT_1_B The Flack x is >> 0 - Do a BASF/TWIN Refinement Please Check

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without
 a literature citation. This should be contained in the
 _exptl_absorpt_process_details field.
 Absorption correction given as empirical
 PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds 0.00673 Ang.

Alert level G

PLAT004_ALERT_5_G	Polymeric Structure Found with Maximum Dimension	1	Info
PLAT007_ALERT_5_G	Number of Unrefined Donor-H Atoms	1	Report
PLAT033_ALERT_4_G	Flack x Value Deviates > 3.0 * sigma from Zero .	0.026	Note
PLAT066_ALERT_1_G	Predicted and Reported Tmin&Tmax Range Identical	?	Check
PLAT791_ALERT_4_G	The Model has Chirality at C8 (Chiral SPGR)	S	Verify
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	27	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density	9	Note

0 **ALERT level A** = Most likely a serious problem - resolve or explain
 2 **ALERT level B** = A potentially serious problem, consider carefully
 2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
 7 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 2 ALERT type 2 Indicator that the structure model may be wrong or deficient
 1 ALERT type 3 Indicator that the structure quality may be low
 3 ALERT type 4 Improvement, methodology, query or suggestion
 2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

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Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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Datablock 1 - ellipsoid plot

